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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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RECRUITING CONTINUES FOR TECHNOLOGISTS

About a year ago the Federal Civil Service Commission began a recruiting drive for technologists. The number of persons on the employment lists now established is not sufficient for today's wartime needs. Accordingly, the Commission has recently reissued the announcement of these opportunities for Government employment, with slightly modified requirements. Salaries for the positions range from $2,000 to $5,600 a year. Applications may be filed until further notice with the Commission's Washington office.

By technologist the Commission means a person experienced in "the necessary production, engineering, and scientific research work essential for the successful operation of an industrial plant, where such plant operation is based upon a thorough and expert knowledge of a branch of an applied science," such as explosives, fuels, plastics, rubber, minerals, or textiles.

For the Junior positions ($2,000 a year), applicants will no longer have to take a written test, and, as before, no written test will be given for the higher positions. The maximum age limit for all the grades has been raised to 60 years.

Copies of the announcement (No. 188), and the forms for applying, may be obtained at first- and second-class post offices, or from the Civil Service Commission, Washington, D. C.

NEW BOOKS AND OTHER PUBLICATIONS

Rubber's Return to the Western Hemisphere. P. W. Litchfield. The Goodyear Tire & Rubber Co., Akron, O. 4 pages.

This pamphlet surveys the recent progress toward rubber production in the New World through *Hevea* and guayule plantations, and the expansion of facilities for making synthetic rubber, together with conservation of crude stocks and increased processing of reclaim. A report of Goodyear plantations in Panama and Costa Rica describes the development of two tracts with a combined area of 3,800 acres, planted with high-yielding stock from the Philippines. [From the *India Rubber World*.]

Rubber Producing Companies—1941. Compiled by the Mincing Lane Tea & Rubber Share Brokers' Association, Ltd., Plantation House, Mincing Lane, London, E.C.3, England. Published by *The Financial Times*, Ltd., 72 Coleman St., London, E.C.2, England. Boards, 5½ by 8¼ inches, 625 pages. Price, 10s. 6d.

Each of the 550 crude-rubber producing companies covered by this manual for investors is described separately in alphabetical order. Four hundred of them are shown in the new simplified style of compilation, and the editor anticipates that this recompilation will be completed in the next edition. The data include: date of registration, a list of directors and secretaries, financial structure, acreage, profits and dividends, balance sheet summary, and other pertinent information. In the preface the editor reports that, for the first eight months of 1941, an average price of about 13½d. per pound had been obtained for crude rubber; that production costs had not exceeded 6d. per pound on most estates, despite increased labor and materials costs; that all companies have made greatly increased profits, a large portion of which has been reserved for taxes. It is also stated that improved cultivation and replanting with budgrafted trees is continuing. [From the *India Rubber World.*]

LET'S LOOK IT UP. Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 134 pages.

This catalog of books on chemistry and related subjects for 1941-42 contains descriptive information on such standard works as "The Chemistry and Technology of Rubber" by C. C. Davis and J. T. Blake, and other volumes of interest to the rubber industry, such as catalysis, colloid chemistry, emulsions, hydrocarbons, plastics, polymerization, protective coatings, rubber chemistry, and synthetic resins. A list of 87 American Chemical Society monographs, most of which are more fully described in the text, is appended. There are lists of new books published in 1941 and others to be published in 1942. Books listed as in preparation include "Colloidal Carbon" by W. B. Wiegand; "Chemistry of Synthetic Resins", Vol. 3, by Carleton Ellis; "Acetylene", by the associates of the late J. A. Nieuwland; and "Surface Energy and Colloidal Systems", by W. D. Harkins and T. F. Young. [From the *India Rubber World.*]

TECHNICAL BOOKS ON ALL SUBJECTS—1942. Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y. 60 pages. Indexed.

This catalog describes books on a variety of technical subjects, including chemistry, rubber, and plastics. [From the *India Rubber World.*]

1942 PLASTICS CATALOG. Published by the Plastics Catalogue Corp., 122 East 42nd St., New York, N. Y. 8½ x 11½ in. 622 pp. $5.00.

The second edition of this catalog, issued annually, brings the data on plastics completely up to date. Every section has been thoroughly overhauled, with the documented facts bolstered by new charts and informative illustrations. The complete story of the role of plastics in the war effort is given in a special section, which includes an informative discussion of how the industry is affected by priorities. Other sections are devoted to materials, plastics engineering, production operations, machinery and equipment, laminates and vulcanized fibres, plastic coatings, and synthetic fibres and rubbers. The Plastics Properties Chart, introduced in the first edition, has been revised and amended, as have the charts on solvents and plasticizers. The section on synthetic rubbers contains descriptions of such products as Thiokol, Neoprene, Ameripol, Hycar, Chemigum and Butyl Rubber, in addition to some of the rubberlike materials, such as Resistoflex, Koroseal and Vistanex. All in all, the catalog offers a wealth of information to anyone connected with, or interested in, the plastics industry in all its many branches. [From *The Rubber Age* of New York.]

PLASTICS IN ENGINEERING (2nd Edition). By J. Delmonte. Published by Penton Publishing Co., Penton Building, Cleveland, Ohio. 6 x 9 in. 601 pp. $7.50.

The first edition of this book, recognized as one of the most outstanding on the subject of plastics, made its appearance less than two years ago. Circumstances and technological developments have so markedly influenced the trends in the plastics industry in the past twenty months, however, that this second edition was essential to keep the records up to date.

Strategic materials, such as brass, zinc, copper, tin, aluminum, magnesium and steel, are now almost wholly restricted to vital war measures. This situation has created a minor revolution in the design of machine parts, as the author points out in his preface, and now, more than ever, manufacturers must become acquainted with ways of adapting plastics to their design programs. With this thought in mind, the data and design information have been completely revised in the new edition so as to be of greatest service to the engineer.

Practically all of the previous chapters have been retained, with several new ones added. The technical data have been reorganized to permit more easy reference to the text material. Extruded plastics and resin-bonded plywoods are given much more prominence because of recent developments in these materials. Among the newer plastics discussed are polyamides, melamine-formaldehyde, polyvinylidene chloride, and methyl cellulose. Useful technical and design data, obtained by the author in his work with the Plastics Industries Technical Institute, are incorporated in the book.

Like other chapters in the book, that on "Synthetic Rubbers and Rubberlike Resins", has been brought up to date. Additions to this chapter include a table on types of synthetic rubber and rubberlike resins, showing the chemical structure (monomer), trade-name of the polymer, and typical applications; a brief discussion of isobutene polymers; and a table giving the physical properties of some of the commercial synthetic rubbers compared with those of natural rubber. [From *The Rubber Age* of New York.]

A.S.T.M. STANDARDS ON RUBBER PRODUCTS. Prepared by A.S.T.M. Committee D-11 on Rubber Products. Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. December, 1941. Paper, 6 by 9 inches, 280 pages. Price, $1.75.

The latest edition of the "A.S.T.M. Standards on Rubber Products" gives 39 specifications and test methods for rubber and rubber products. It includes several new standards, first issued during 1941, and incorporates numerous revisions of standards previously issued or approved.

There are 19 general methods, covering chemical analyses, sample preparation, accelerated aging, adhesion, hardness, tension, compression-set, abrasion-resistance, ply-separation, cracking, resistance to light-checking, state of cure (T-50), compression-deflection characteristics, indentation, etc. Included in this section are two tentative tests (Tear Resistance of Vulcanized Rubber, and Compression Fatigue of Vulcanized Rubber) first issued in 1941; and proposed drafts of tests for Accelerated Light-Aging of Rubber Compounds, and Calibrating a Light Source Used for Accelerating the Deterioration of Rubber.

Five standards for rubber hose and belting include a tentative method of testing automotive airbrake and vacuum brake hose newly issued. Four specifications for rubber gloves, matting, and tape, and a testing method and five specifications for insulated wire and cable are given. Tentative methods for sampling and testing rubber latex and asphalt composition battery containers, both issued in 1941, are contained in the section on Latex, Rubber Cements, Sponge, and Hard Rubber Products.

An 11-page classified bibliography reports important recent sources of information on the properties and testing of rubber, and there is a list of the personnel and subcommittees of Committee D-11. [From the *India Rubber World.*]

1941 Supplement to A.S.T.M. Standards Including Tentative Standards. Part 3, Nonmetallic Materials—General. Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. December, 1941. Cloth, 6 by 9 inches, 641 pages. Price, $3.

This latest supplement contains about 150 specifications, definitions, and tests, either issued for the first time in 1941 or revised, and covers the following materials: coal and coke, petroleum and lubricants, electrical insulating materials, plastics, rubber products, textiles, paper, soaps, etc.

The 15 methods of testing rubber and rubber products, latex, and sponge, and the three specifications for rubber insulated wire and cables are also reported in "A.S.T.M. Standards on Rubber Products". Eleven tentative methods of testing plastics for flammability, color-fastness to light, impact-resistance, tension, and other properties are given.

The 1941 supplement is the last that will be issued. A complete new book of standards will be prepared in 1942. [From the *India Rubber World.*]

Advances in Colloid Science. Vol. 1. Edited by E. O. Kraemer, in collaboration with F. E. Bartell and S. S. Kistler. Published by Interscience Publishers, Inc., 215 Fourth Ave., New York, N. Y. 6 x 9 in. 434 pp. 161 illustrations. $5.50.

This book covers recent significant discoveries or advances in colloid science, either experimental or theoretical. It is the first of a planned series of volumes intended to provide a medium in which these advances will be presented in a more comprehensive and unified fashion than is possible in regular technical periodicals. Reviews of developments in the various branches of the vast colloid field will be entrusted to technologists closely associated with, and contributing to, technical knowledge of that field.

In the current volume, for example, twelve separate subjects are presented, titles and contributing authors being as follows:

The Measurement of the Surface Areas of Finely Divided or Porous Solids by Low Temperature Adsorption Isotherms, by P. H. Emmett.

The Permeability Method for Determining Specific Surface of Fibers and Powders, by R. R. Sullivan and K. L. Hertel.

A New Method of Adsorption Analysis and Some of Its Applications, by Arne Tiselius.

Solubilization and Other Factors in Detergent Action, by James W. McBain.

Recent Developments in Starch Chemistry, by Kurt H. Meyer.

Frictional and Thermodynamic Properties of Large Molecules, by R. E. Powell and Henry Eyring.

The Constitution of Inorganic Gels, by Harry B. Weiser and W. O. Milligan.

The Creaming of Rubber Latex, by G. E. Van Gils and G. M. Kraay.

Streaming Birefringence and Its Relation to Particle Size and Shape, by John T. Edsall.

Synthetic-Resin Ion Exchangers, by Robert J. Myers.

The Study of Colloids with the Electron Microscope, by Thomas F. Anderson.

Anomalies in Surface Tensions of Solutions, by Ernst A. Hauser.

The chapter on the creaming of latex, contributed by Van Gils and Kraay, both associated with the Department of Rubber Research of the Experimental Station West-Java in Buitenzorg, includes data on creaming in actual practice, the creaming mechanism, factors affecting creaming, and recent research. The

work of the authors in this field is especially stressed, with due note of contributions by other latex technologists. Like all other chapters in the book, this chapter includes a comprehensive bibliography.

If this first volume is any criterion of others to follow in the series, then the entire series will prove most valuable to research and other workers in the field of colloid science. It has been well prepared, carefully edited, and has complete author and subject indexes. [From *The Rubber Age* of New York.]

HANDBOOK OF CHEMISTRY AND PHYSICS. Twenty-fifth Edition, 1941-42. Charles D. Hodgman, Editor-in-Chief, and H. N. Holmes, Associate Editor. Published by Chemical Rubber Publishing Co., 2310 Superior Ave., Cleveland, O. Fabrikoid, $4\frac{3}{4}$ by $7\frac{1}{2}$ inches, 2521 pages. Indexed. Price $3.50.

Much new or completely revised material is contained in the latest edition of this standard reference book for physicists and chemists. The section on Properties of Commercial Plastics, revised for the 1939 edition, has been checked to assure up-to-date information on developments in this growing industry. A 15-page table of natural secants and cosecants for convenience in machine computation augments the mathematical section. The abbreviations and symbols have been completely revised on the basis of a list proposed by the Committee of the American Association of Physics Teachers. Other revised or new matter incorporated in this edition for the first time places the data in accord with the results of recent scientific investigation. [From the *India Rubber World.*]

A CENTRAL ORGANIZATION FOR FUNDAMENTAL RESEARCH ON RUBBER *

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Far-sighted leaders of the rubber industry have long recognized the need of more research on rubber, particularly research of a broad, fundamental character. Ambitious plans have been proposed from time to time for the sponsoring of such research by the rubber industry. The usual history of these plans is that they have been ably presented, discussed at length, and ultimately allowed to lapse. This paper, reviving the subject, is the outcome of a conversation with the forward-looking editor of *India Rubber World*, and is here presented at his suggestion in the hope that it may lead to new interest and ultimately to some tangible accomplishment.

The present plan, which involves no essentially new or original features, is that a relatively small, but strong, central organization be created to undertake difficult, long-term, fundamental research on rubber and, at the same time, to promote research in universities and in industry by coöperation through the dissemination of information and by other means.

THE PRESENT STATUS OF FUNDAMENTAL RESEARCH ON RUBBER

Before presenting a sketch of the proposed organization, it is in order to take stock of the present resources for research. Any new plan that may be proposed should meet an actual need, and should be designed to supplement the research now being done rather than to uproot and rebuild the present organizations.

The present situation regarding fundamental research on rubber can be presented in simple form by asking and answering certain relevant questions. What is fundamental research? Where is fundamental research on rubber now being done? Who is doing it? Wherein are the present accomplishments inadequate?

1. DEFINITION OF FUNDAMENTAL RESEARCH

Fundamental research is the obtaining of scientific data and the formulation of broad, underlying scientific principles. It is motivated by scientific curiosity and is undertaken without thought of immediate application or early financial return.

Applied research, on the other hand, generally relates to projects of a specific and often confidential nature, with a definite commercial objective requiring an early solution of the problem. Some applied research, however, is broad in scope and thorough in method, and differs from fundamental research only in that it is motivated by the hope of reaching practical ends. This type of work has been aptly designated as pioneering applied research.

Numerous fascinating examples of the different kinds of research are cited in two recent publications of the National Resources Planning Board entitled "Research—A National Resource. I. Relation of the Federal Government to Research.

* Reprinted from the *India Rubber World*, Vol. 105, No. 3, pages 255-258, December 1, 1941.

II. Industrial Research."* These publications, which were prepared by a number of prominent scientists and industrial leaders, contain a wealth of information about the problems, personnel, organization and management, expenditures, and typical accomplishments of government and industrial organizations for research.

2. Organizations Engaged in Fundamental Research

Contributions to the basic knowledge of rubber come from a great number and variety of organizations the world over. No one country and no one type of organization have a monopoly on research. The results of most fundamental investigations on rubber, and many applied investigations as well, are published in Rubber Chemistry and Technology. The principal sources, in the United States, of papers which appear in this periodical are firms producing compounding ingredients and synthetic rubber, manufacturers of rubber goods, universities and colleges, users of rubber products, and government bureaus.

Most of the research done in the university and the government laboratories is fundamental. Some of the contributions from industrial laboratories are fundamental research; more of them, however, represent pioneering applied research, and still more, simple applied research.

The foreign papers in Rubber Chemistry and Technology come from similar sources and, in addition, from institutions for research on rubber which find no counterpart in the United States, such as the Rubber Research Institute of Malaya or the Netherlands Government Rubber Institute. Three new institutions have been created within recent years in connection with the International Rubber Regulation Agreement, and have as their objective the development of new and increased uses for rubber. One of these organizations, the British Rubber Producers' Research Association, has undertaken a broad program of fundamental research as a long-term means of increasing the consumption of rubber. This program is being followed in spite of the war, and, although work appears to have gotten under way only last year, eleven substantial papers have already been published.

Fundamental research is being sustained in Germany also. Some of the papers which are being published in German rubber journals deal with projects which a practically minded American budget committee would regard as academic luxuries, even in time of peace.

3. Personnel Engaged in Research

Some of the fundamental research on rubber is done by fortunately situated individuals who are privileged to work in well-equipped laboratories and devote their whole time to research. Much of the research, however, is done by busy individuals who have numerous other duties. Sometimes it partakes of the nature of a hobby or an avocation. In nearly all cases research, like other creative work, is done by men who are genuinely interested in it and want to do it even to the point of making sacrifices for the privilege.

The men themselves who do research on rubber come from all ranks, and differ widely in qualifications and abilities. In the author index of Rubber Chemistry and Technology, some of the highest salaried executives of the industry rub shoulders, figuratively speaking, with junior laboratory assistants and apprentices; while the president of a great university is accorded no distinction over teachers from small colleges.

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* Copies may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. The price of the first is 50¢, and the second, $1.

4. Inadequacy of the Present Research

The principal trouble with fundamental research on rubber, as it is now done, is that there is not nearly enough of it. The effort devoted to obtaining new knowledge is disproportionately small in comparison with the large amount of time and money which are spent in applying existing knowledge. In the year 1937, for example, it was estimated that 2,518 persons in the rubber industry in the United States were engaged in research. In the same year only about 20 research papers published in the United States might be classed as representing either fundamental or pioneering research. There were approximately 30 authors, a third of whom were employed in university and government laboratories.

Another difficulty is that sufficient attention is not now given to problems which call for long study, extensive equipment, and the coördinated effort of men having different types of training. A great deal of valuable research can be done by individuals, even when working alone and for part time, but there is an increasing need, with the growth of science and industry, of group research by a well coördinated organization.

OBJECTIVES OF PROPOSED ORGANIZATION

To meet the needs pointed out in the foregoing paragraphs, it is suggested that the proposed organizations have as its primary objective the conducting of long-term, fundamental research and, as a secondary objective, the stimulation of research elsewhere by coöperation with other organizations, by the dissemination of information, and by a campaign of education.

1. Program of Research

The problems for study by the organization should be chosen from the standpoint of providing systematic, scientific knowledge of rubber. In deciding among numerous possible lines of investigation, the question should be asked: "Which investigations are the most likely to open up a significant and hitherto unexplored body of knowledge regarding rubber?"

In undertaking to answer this question, it would be desirable to make a systematic survey of the constants, properties, reactions, and types of behavior of rubber. The perennial lists of "unsolved Problems of the Rubber Industry" would probably be of little help because most of the problems in such lists call for applied rather than fundamental research; furthermore, the important discoveries to be made regarding rubber are discoveries which are not anticipated.

It is characteristic of fundamental research that the ultimate value of the work often lies in results which were not the immediate objectives of the investigation and could not have been anticipated any more than our vast oil fields could have been anticipated by the early Spanish explorers who prospected the very regions looking vainly for gold and silver. Large and important discoveries are often said to come by chance. Serendipity, however, is a better word than chance, since it implies that the investigator must be alert and open-minded enough to realize the significance of an unexpected observation.

To give research workers latitude to follow up new and unexpected developments, it would seem desirable for the managing board of the organization to decide only on the general fields for investigation and leave specific projects and methods to the workers. The board, for example, might decide on the study of the electrical behavior of rubber, but the decision as to the amount of attention which would be paid to piezoelectrification, dielectric strength, or electric moments would rest with the research men themselves.

2. Information Service

The giving of information is logically a function of a research organization. Investigational work requires a wide and thorough acquaintance with the literature. Research men must of necessity accumulate a large store of general and background knowledge of the entire field of rubber science and technology. When this knowledge is in hand and is well organized, it can be passed on to others with relatively little effort and expense. A great deal of research could be stimulated in small and isolated laboratories by making available to them information and literature on the problems in which they are interested. An information service might easily justify its cost by saving some of the time and money which are spent in the needless rediscovery of facts and principles already recorded in the literature.

A distinction would, of course, have to be made between the giving of information and trouble-shooting. The unfortunate experience of other research organizations has shown that where trouble shooting is undertaken as a secondary activity, it almost invariably encroaches on research to such an extent as to become the major activity.

The development of the information service could be facilitated by coördinating it with the well known Information Bureau of the Research Association of British Rubber Manufacturers and avoiding any unnecessary duplication of services or activities.

3. Coöperation with Universities in Research

The proposed organization could stimulate a wide variety of fundamental research by collaborating with colleges, universities, and other institutions in problems which lie on the borderline between rubber investigations and other fields. For example, an academic investigator in some special field such as x-ray diffraction, spectroscopy, or magnetic susceptibility may wish to make some measurement on rubber, but may be handicapped by the lack of suitable specimens and by unfamiliarity with the general properties and behavior of rubber. It would be a relatively easy matter, then, for a well-equipped organization doing research on rubber to supply the necessary background information and provide adequate material for experimental needs. Such collaboration would lead to more and better research work than either party could do alone.

4. Stimulation of Research in Industry

An organization of the type here contemplated would occupy a position of leadership in fundamental research and, in this position, could conduct properly a sustained campaign of education to promote a better appreciation of the value of research on the part of industry. In the industry many able research men are advanced to administrative positions on account of the ability which they have shown in research, but in the higher positions they are barred by circumstances from further scientific accomplishments. A few hardy scientists who have risen to high places in the rubber industry have continued to do noteworthy research, but the majority have been lost to science.

This loss is large and unnecessary, because many of the men could do worthwhile research in a part of their time. Furthermore their value as administrative officers would be increased in the long run by their maintaining their scientific interests and point of view. Any one who doubts the practicability of part-time research should consider the average university professor who teaches, writes textbooks, participates in public affairs, and serves on endless committees, but

nevertheless finds or makes time for fundamental research. Research is a tradition of the universities; it should become a tradition of industry as well.

The proposed organization could check another and even more needless waste by encouraging the publication of valuable fundamental data obtained in connection with practical studies. Such data are sometimes buried in company files, because policies do not permit the publication even of work of wholly academic interest. More often, however, the failure to publish arises from the fact that the firm does not allow the research man who has done the work enough time to round out and write up the results in a form acceptable for publication.

REQUISITES OF AN ORGANIZATION FOR FUNDAMENTAL RESEARCH

An organization for fundamental research differs greatly from an organization set up for business or manufacture. Research cannot be done on an assembly-line basis. Some of the very methods by which a business may be run successfully will wreck a research organization. Some general principles can be laid down which must govern the formation and management of the proposed organization if it is to accomplish its intended purpose. Wholehearted acceptance of these principles will go far toward assuring the success of the organization, irrespective of how many of the details may be worked out.

1. The Organization Should Be Made Up of Research Men of Superior Ability

A prime requisite of an organization to undertake difficult fundamental research is that it should attract and hold men of superior ability. A relatively small group of such men could accomplish more of the type of work here contemplated than a large staff of mediocre individuals. Able research men are hard to get, so a new organization would have to make a small beginning and get under way slowly. Fortunately the proposed organization could offer inducements relating to the nature of the work and the working conditions which would have more weight with the type of men sought than salary alone.

The research staff should be selected not only from a consideration of the qualifications of the individual men, but also with a view to building up a unit or units comprised of men having supplementary types of training. In some cases men of the qualifications sought cannot be found, but will have to be developed.

2. The Organization Should Have Stability

Research always requires a great deal of time. The broader and the more fundamental the research, the less practical it becomes to push it through to completion according to a predetermined schedule. To allow time for thorough and unhurried work to be done, the proposed organization should be managed and financed with the utmost regard for stability. A modest budget assured over a period of years would be vastly preferable to a large annual budget in which the allotment for each project had to be justified by the showing made during the previous year. Sure-fire projects which can be counted upon to make a good showing in a relatively short time represent a type of work which the proposed organization should shun.

3. The Management Should Consist of Men Trained in Science

Since the requirements of research are so different from those of business or production, the board of directors or the committee set up to administer the

affairs of the proposed organization should be made up of men who have themselves been trained in science and are sympathetic toward fundamental research. Fortunately there are such men among the leaders of the rubber industry.

4. The Organization Should Be Associated with a Large Scientific Institution

Any program of fundamental research on rubber will require an extensive background in all the natural sciences; hence the proposed organization should be connected with a large institution for scientific research so that its staff could associate freely with specialists in the various fields of physics, chemistry, mathematics, and engineering. The library, laboratory, and shop facilities of the large institution would, of course, be far more extensive than those which any research unit could hope to maintain independently. There are several universities and institutions for research and at least one government bureau which might afford a suitable location for the proposed organization.

ESTABLISHMENT OF THE PROPOSED ORGANIZATION

The present discussion has been intentionally confined to presenting the need of active support of fundamental research and pointing out how a strong, central organization might effectively meet this need. The experience of other industries has indicated that when the importance of fundamental research is realized, means will be found for setting up and maintaining an adequate organization for conducting the research. The Textile Foundation and the American Petroleum Institute, for example, were established under different circumstanaces and operate under different plans, but both function very effectively in getting fundamental research done.

The support of an organization for fundamental research should present no serious problem to the rubber industry. An annual budget of, say, $100,000 would represent a large outlay as expenditures for fundamental research go, but it would amount to only about 1 per cent of what the industry is now spending for applied research and would represent less than 0.01 per cent of the annual volume of business of the industry.

If the American rubber industry can be brought to realize the potential value of fundamental research, it has able leaders who can initiate an adequate organization for research, and it possesses ample resources from which to provide the necessary support.

INDUSTRIAL PROGRESS IN SYNTHETIC RUBBERLIKE POLYMERS *

HOWARD I. CRAMER

SHARPLES CHEMICALS INC., PHILADELPHIA, PENNA.

The developing emergency in the Pacific is focusing attention on our capacity to produce synthetic rubber. When we consider that 97 per cent of our crude rubber is imported from British Malaya, the Netherlands Indies, Ceylon, and adjacent territories in the Far East, the seriousness of our position with respect to the supply of this vital raw material is evident. The gravity of the situation was reflected in the action of the Office of Production Management, on June 20, 1941, placing rubber and rubber products under priority to conserve the supplies of crude rubber now in this country and, at the same time, build up a reserve against the threat of a possible stoppage of shipments from the Orient. Conservation, however, is only a stopgap measure and, in the event of a protracted conflict, we would turn inevitably to new plantations in Central and South America and to our small but rapidly expanding synthetic rubber industry for new sources of supply.

Important questions of interest to the general public, today, therefore, are: How much synthetic rubber are we now producing? To what extent can it be used to replace natural rubber? How much time would be required to build larger plants capable of producing an appreciable proportion of our normal requirements?

In addition, the technical man outside the rubber industry is interested also in the following questions: How are the synthetic rubbers produced? Can they be produced at cost levels which will make them competitive with natural rubber? What are their processing qualities and how do products manufactured from them meet the laboratory and performance specifications set up for articles made from natural rubber?

The purpose of this paper is to review the progress being made in this country in the manufacture of synthetic rubber, and in so doing attempt to answer the above questions.

In 1839 Charles Goodyear discovered the process of vulcanization whereby natural rubber, or caoutchouc, is converted into products useful to man. Almost at once chemists undertook the search for a synthetic substitute. The versatile Faraday[11] in 1826 had already demonstrated that rubber was essentially hydrocarbon in nature and that its empirical formula was C_5H_8. In 1860 Williams[27] broke rubber down by pyrolysis to give a water-white, mobile, low-boiling liquid of the same composition as rubber, which he named isoprene. Fifteen years later Bouchardat[4] converted this isoprene into an elastic mass and postulated for the first time the monomerpolymer relation existing between this material and rubber.

The story has been traced from this point up to the present by Whitby and Katz[26] and by Wolf and Wolf[28]. Suffice it to point out here that, from the time of Bouchardat on, the search for a synthetic product waxed hot as the price of rubber reached high levels and waned as it went down. The greatest progress,

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except that of recent years, was probably made in the decade preceding the first World War. During this period large organized research groups in England and Germany competed with each other in a mad race to be the first to achieve a commercial synthetic rubber. Rubber at $3.00 per pound in 1910 spurred them on. The most tangible accomplishments of this period were (1) the development by the English groups in collaboration with Auguste Fernbach, of the Pasteur Institute, of a process for the fermentation of starch to give acetone and a series of higher alcohols, and (2) the discovery by the German group of organic accelerators of vulcanization, independently of the discovery of these compounds in the United States. Both groups did evolve workable processes for the production of isoprene and several of its homologs, and for their polymerization induced by heat or by catalysts, such as sodium. The products, however, were of poor quality, and had inferior elasticity and resistance to aging and wear. The English despaired of ever finding a complete solution of the problem, and concentrated their energy on the development of their rubber plantations in the Far East. The Germans put their process on the shelf until about 1915 when, as a result of the English blockade, their supply of natural rubber ran low. Faced with this emergency, they built and operated for the duration of the war a synthetic rubber plant which had a capacity of 150 tons per month of inferior product.

In the early twenties the British put into effect the Stevenson plan, which restricted the output of their plantations. Rubber began to rise in price, with the result that many laboratories in the United States and Europe took up the quest again. By 1926 the production of the Dutch plantations began to become a factor in the market, and rubber prices tumbled. Once more all laboratories except those of the I. G. Farbenindustrie in Germany and of du Pont in the United States abandoned work on synthetic rubber. The work in Germany resulted in a flood of patents, but by 1930 the quality, wherever produced, was still very inferior to rubber.

Why, after so many years' effort, was this true? One explanation was that, without exception, chemists had been following the principle used in the successful synthesis of alizarin and other natural products—namely, to duplicate the composition of the natural substance. This approach in the case of rubber failed, apparently because, in spite of years of intensive research, the exact molecular configuration of rubber, the mechanism of polymerization whereby isoprene is converted into natural rubber, and the way nature is able to perfect this polymerization, remain essentially unknown.

In any event, a truly rubberlike polymer was not realized until chemists abandoned the time-honored approach and struck out to develop new polymers which, although they might possess the essential properties of the natural product, would be derived from monomers distinctly different in chemical composition from isoprene. No synthetic polymer of isoprene has yet been produced which approaches natural rubber in quality, or is even comparable with the commercial synthetic rubbers now being produced. The first successful product resulting from this approach was polychloroprene. Although physically its structure must approach that of natural rubber, chemically it contains 40 per cent chlorine which is not a constituent of the natural product at all. This synthetic product was developed in the du Pont laboratories, but really represented the fruition of a lifetime of pure research by one man who had no more than a casual interest in rubber. This man was Julius Nieuwland, professor of chemistry at the University of Notre Dame, and the subject of his life's studies

was acetylene. In 1925 he presented a paper describing some new derivatives of this compound before a group of chemists at Rochester. In his audience was Elmer Bolton, of the du Pont laboratories, who had been engaged on the problem of synthesizing rubberlike polymers. In Nieuwland's results he saw a possible solution to the problem. From that point on, a du Pont research group, headed by the late Wallace Carothers[6-9] took over, after the necessary patent and royalty arrangements had been made. The result was Duprene, now called Neoprene, which was first disclosed to the rubber industry in a meeting of the Akron Section of the American Chemical Society in 1931. With the success of this first American attempt, the spell seemed to have been broken, and encouraging developments followed in steady succession.

In 1932 Thiokol, an alkylene polysulfide elastic developed by Patrick[17, 18], was introduced commercially. In 1933 the first patent on Koroseal, a plasticized polyvinyl chloride possessing many of the desirable properties of rubber, was granted to Semon[21]. Germany announced in 1935 the commercial production of the Buna synthetic rubbers, the basic ingredient of which is butadiene. In 1938 the German army rolled into Austria on tires made from this synthetic rubber, and proved to the world that a practical synthetic product was a reality. With the spreading of the present World War over Europe and toward the Far East, the United States at last began to become concerned over its supply of crude rubber. As if in answer to the question in the public mind as to how we could become independent of the Far East source of supply, there followed in 1940 in quick succession announcements by Goodrich, Goodyear, Firestone and Standard Oil of New Jersey, of new variations of the butadiene-derived type of synthetic rubber.

CLASSIFICATION OF SYNTHETIC RUBBERS

In consequence, there is being produced today in the United States a greater variety of synthetic rubbers or synthetic elastics than in any other country, including Germany.

This variety of different types of synthetic elastics may be classified, together with producing companies, as follows:

I. "True" synthetic rubbers or elastoprenes, derived from butadiene or its homologs or its substituted derivatives—unsaturated
   - *A.* Simple butadiene polymers (none produced in the United States)
   - *B.* Modified butadiene polymers
     1. Butadiene plus styrene (Buna-S, Standard Oil Company of New Jersey and Firestone Tire & Rubber Company)
     2. Butadiene plus acrylonitrile (Buna-N or Perbunan, Standard Oil Company of New Jersey and Firestone Tire & Rubber Company; Ameripol or Hycar,* B. F. Goodrich Company; Chemigum,* Goodyear Tire & Rubber Company)
   - *C.* Substituted butadiene polymers
     1. Polymers of isoprene (none produced in the United States)
     2. Polymers of methylisoprene (none produced in the United States)
     3. Polymers of chloroprene (Neoprene, E. I. du Pont de Nemours & Company, Inc.)
   - *D.* Modified butene polymers
     1. Butenes plus small amounts of butadiene or other diolefins (Butyl Rubber, Standard Oil Company of New Jersey)

II. Synthetic rubberlike elastics or elastoplastics—saturated
   - *A.* Polyalkanes
     1. Polybutene (Vistanex, Standard Oil Company of New Jersey)
     2. Polyphenylene ethylene (A. X. F., United States Rubber Company)

* Identity not disclosed by the manufacturer but reported to be of the type indicated.

B. Polyvinyl derivatives
1. Polyvinyl alcohols (P. V. A. series, R. & H. Chemicals Department, du Pont company)
2. Polyvinyl acetate-chloride (Vinylite copolymers, Carbide & Carbon Chemicals Corporation)
3. Polyvinyl chloride (Koroseal, B. F. Goodrich Company; Vinylite-Q, Carbide & Carbon Chemicals Corporation; Flamenol, General Electric Company)
4. Polyvinylidene chloride (Saran, Dow Chemical Company)
5. Polyvinyl acetals
   a. Polyvinyl alcohol plus formaldehyde (Formvar, Monsanto Chemical Company)
   b. Polyvinyl alcohol plus butyraldehyde (Butvar, Monsanto Chemical Company; Vinylite-X, Carbide & Carbon Chemicals Corporation; Butacite, du Pont Company)

C. Reaction products of aliphatic dihalides plus alkali polysulfides
1. Ethylene dichloride plus sodium tetrasulfide (Thiokol-A, Dow Chemical Company)
2. Dichloroethyl ether plus sodium tetrasulfide (Thiokol-B, Dow Chemical Company)

D. Miscellaneous elastoplastics
1. Plasticized polyacrylic esthers (the Acryloids, Röhm & Haas Company)
2. Mixed alkyd condensation products (Duraplex, Röhm & Haas Company)

The above classification is purely arbitrary because there is no standard definition of just what constitutes a synthetic rubber[1, 12]. Included in the first main group are those polymeric products whose chemical structures are closely related to that of natural rubber. However, because no commercial products are being derived from isoprene, it is preferred to define the group as derivatives of butadiene, the parent hydrocarbon of the entire series of diolefinic hydrocarbons.

In the second group are found those elastic polymers which are distinctly different from natural rubber in chemical structure. Most of these products exhibit the properties of both elasticity and plasticity, and hence have been termed "elastoplastics". With the exception of the Thiokols, they are not vulcanizable. All are thermoplastic.

To include such a wide range of elastic polymers in the above classification is not inconsistent with the broad concept of Schade[19]:

"The meaning of the word rubber has changed. It no longer signifies a particular hydrocarbon material, but has been widely adopted to characterize a class of substances similar physically to natural rubber, regardless of their chemical composition. In order to qualify as a rubber, a material should stretch readily to a considerable degree and, after release, retract forcefully and quickly; but no specific criteria have been generally accepted limiting the values for these properties."

On the basis of this broad concept, an appreciable number of the softened or so-called plasticized synthetic resins might also be classed as synthetic rubbers or elastics.

STRUCTURAL RELATIONS

The structural relations of several of the principal types of polymers to one another and to the monomeric substances from which they are derived, either by polymerization or condensation, are given in Table I, taken in part from the review by Wood[29].

SYNTHESIS OF THE PRINCIPAL TYPES

The manufacture of any one of the synthetic rubbers involves two main processes—the synthesis of the monomeric raw materials, and their conversion by polymerization or condensation to give the final polymer. The polymerization methods employed have been (1) mass polymerization over a catalyst of the monomer, liquid or gaseous or in solution in an organic solvent, preferably an aromatic hydrocarbon, and (2) emulsion polymerization. The first method was used in Germany and Russia, and also formerly in the production of Neoprene. It has been almost completely superseded in this country by the emulsion process. The extensive research carried out by the Germans in the reconstruction period following the first World War proved to them that isoprene did not give a satisfactory synthetic rubber. Furthermore, all methods for its synthesis were complicated and expensive. They then turned to butadiene, and found that it gave a satisfactory product when polymerized over metallic sodium as the catalyst. The combination of the first syllables of the two words, butadiene and natrium (the Latin for sodium), gave the trade name adopted in Germany for this whole series—namely, the "Bunas". Another major advance made by German investigators was to add other diolefins and a variety of vinyl compounds to the butadiene before polymerization to give "copolymers". The emulsion polymerization technique was developed by them for the manufacture of this type of polymer, and has now been adopted universally in the United States.

Whereas in Germany butadiene is prepared by the classic limestone-coke-acetylene route, our main source has been and undoubtedly will continue to be petroleum. The principal methods employed on a commercial basis in the United States for the synthesis of butadiene are indicated by these equations:

1. $\text{Petroleum} \xrightarrow[\text{cracking}]{\text{normal}} CH_2{=}CH{-}CH{=}CH_2$ (1/2 to 3/4%)

   $\text{Petroleum} \xrightarrow[\text{cracking}]{\text{special}} CH_2{=}CH{-}CH{=}CH_2$ (5 to 12%)

2. $CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\overset{Cl}{C}H{-}\overset{Cl}{C}H{-}CH_3$

   $CH_3{-}\overset{Cl}{C}H{-}\overset{Cl}{C}H{-}CH_3 \xrightarrow[\text{heat}]{BaCl_2} CH_2{=}CH{-}CH{=}CH_2 + 2HCl$

3. $CH_3CH_2CH_2CH_3 \xrightarrow[600^\circ\,C]{Al_2O_3\text{–}Cr_2O_3} CH_3{-}CH{=}CH{-}CH_3 + H_2$

   $CH_3{-}CH{=}CH{-}CH_3 \xrightarrow[650^\circ\,C]{Al_2O_3\text{–}Cr_2O_3} CH_2{=}CH{-}CH{=}CH_2 + H_2$

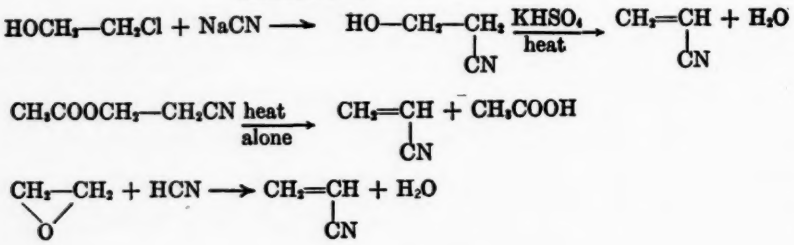
4. $2HC{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CH{-}C{\equiv}CH$

   $CH_2{=}CH{-}C{\equiv}CH \xrightarrow[\text{hydrogenation}]{\text{selective}} CH_2{=}CH{-}CH{=}CH_2$

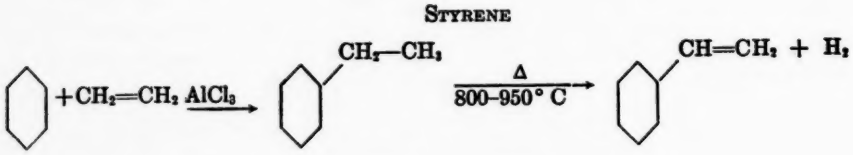
The principal secondary monomers used with butadiene in the production of the copolymeric products are acrylonitrile and styrene. Methyl methacrylate is

used to a lesser extent, in this case in the formation of ternary polymeric systems. The outstanding syntheses for these monomers follow:

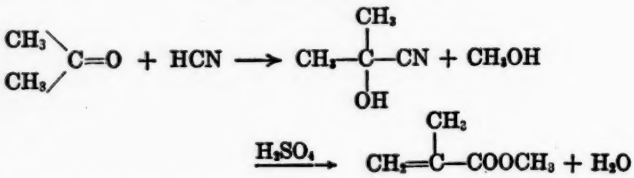
ACRYLONITRILE



STYRENE



METHYL METHACRYLATE



The emulsion polymerization processes for the conversion of mixtures of these monomers into synthetic Buna latices stem from the I. G. Farbenindustrie patents of Tschunkur, Bock, and Konrad[3, 16, 25]. Many improvements in their original methods have been made in this country, the majority of which are only beginning to be disclosed in the patent literature. In the operation of this process, the mixture of butadiene and comonomer(s) is emulsified with water, with the aid of a soap or other wetting agent. To this emulsion are added small quantities of polymerization catalysts and of certain modifying agents which, it is claimed, exert a directing influence on the course of the polymerization, favoring the formation of linear polymers, as well as a determinitive effect on the degree of polymerization. The polymerization catalysts are usually oxidizing agents, such as hydrogen peroxide, sodium perborate, ammonium persulfate, or organic peroxide or peracids.

Modifying agents used are carbon tetrachloride, hexachloroethane, and other organic halogen compounds, trichloroproprionitrile, and sodium cyanide. Organic sulfur compounds, such as mercaptans, xanthogen disulfides, thiuram disulfides, and sulfinic acids, are particularly effective agents for this purpose, according to recent patents.

The emulsified reaction mixture is heated at 40-60° C for a period sufficient for the completion of the polymerization, which is normally 10-15 hours, depending on the temperature employed.

The resulting synthetic latex behaves similarly to natural latex. It may be used as such in many dipping operations, or it may be coagulated with an acid or a polyvalent salt, depending on the type of emulsifying agent used, to give a

coagulum that is washed on a mill, dried, and massed in much the same fashion as that from natural latex.

Unlike natural rubber, however, the final product tends to continue to polymerize on standing. This results in a hardened polymer, which is difficult to process. To retard this change, polymerization inhibitors, such as phenyl-β-naphthylamine or other typical antioxidants for rubber of the diaryl amine type, are added to the polymerizate before the final processing steps.

The physical and processing qualities of the polymer depend on the length of the linear chain developed and on the extent to which cross-linked polymer is formed as opposed to linear polymer. These components of the polymerization can be controlled to a certain extent by the temperature employed, the polymerization catalysts and modifying agents used and, what is probably the most vital, the purity of the monomers going into the process.

A typical reaction mixture employed in the emulsion process is:

Butadiene	60-75	Polymerization catalyst	0.1-1.0
Styrene or acrylonitrile	40-25	Modifying agent	0.1-1.0
Emulsifying agent	1-5	Water	100-250

The proportion of styrene or acrylonitrile used may be varied over a rather wide range, *i.e.*, from 25 to 40 per cent. The amount normally used is in the neighborhood of 25 per cent.

The development of the various polymers of β-chloroprene which now appear under the name of Neoprene is described in the publications of Carothers and associates[6-9]. The monomer is prepared according to the following synthesis:

$$2HC{\equiv}CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2{=}CH{-}C{\equiv}CH + HCl \longrightarrow \overset{Cl}{\underset{|}{CH_2}}{-}CH{=}C{=}CH_2 \longrightarrow$$

$$CH_2{=}\overset{Cl}{\underset{|}{C}}{-}CH{=}CH_2$$

Its polymerization to α-polychloroprene, which resembles unvulcanized rubber, is effected by the emulsion method. It has been reliably stated that some of the recent types of Neoprene represent copolymers of chloroprene with other monomeric substances.

The method of polymerization employed in the production of Butyl Rubber has not been disclosed. This product has been described as a "copolymer of olefins with small amounts of diolefins". The proportion of diolefinic component is unusually low. Specifically, the amount used is sufficient to give a residual unsaturation after polymerization which is equivalent to 1-2 per cent of that of natural rubber.

The organic polysulfides sold under the name of Thiokol are representative of the condensation polymers and also of the elastoplastics. They are formed by the reaction in aqueous medium of an organic dihalide with sodium tetrasulfide. The reaction product may be obtained as a suspension of rather large particle size, which may be coagulated with acid and processed in a manner somewhat similar to that for rubber latex.

In the resulting product, two of the four sulfur atoms present are liable and

may be removed by treatment with sodium hydroxide. The reactions involved in these changes for the product derived from dichloroethyl ether are :

$$ClCH_2—CH_2—O—CH_2—CH_2Cl + Na_2S_4 \longrightarrow \left[—CH_2—CH_2—O—CH_2—CH_2—\underset{\underset{S}{\|}}{S}—\underset{\underset{S}{\|}}{S}—\right]_n$$

Thiokol B

$$\left[—CH_2—CH_2—O—CH_2—CH_2—\underset{\underset{S}{\|}}{S}—\underset{\underset{S}{\|}}{S}\right]_n + NaOH \longrightarrow \left[—CH_2—CH_2—O—CH_2—CH_2—S—S—\right]_n$$

Thiokol D

A number of the thermoplastic synthetic resins can be plasticized or softened ("elasticized" would be a more appropriate term) by the addition of specific high-boiling liquids to give elastic products possessing good extensibility and fair elasticity. The polyvinyl derivatives have been exploited to the greatest extent in this manner; included are the alcohol, chloride, copolymer of chloride and acetate, and finally the various acetals. Of this group, the plasticized polyvinyl chlorides offered under the generic name of Koroseal has received the greatest attention by the rubber industry. The monomeric material may be produced by any of the following methods:

1. $ClCH_2—CH_2Cl + NaOH \longrightarrow HOCH_2—CH_2Cl + NaCl$

   $HOCH_2—CH_2Cl \longrightarrow CH_2=CHCl + H_2O$

2. $CH\equiv CH + HCl \xrightarrow{\text{catalyst}} CH_2=CHCl$

3. $CH_2=CH_2 + Cl_2 \xrightarrow[\text{temperature}]{\text{elevated}} CH_2=CHCl + HCl$

In this case polymerization may take place either in organic medium or, according to recent work, in aqueous medium. The resulting hard, hornlike, thermoplastic polymer is plasticized by the addition on an ordinary rubber mill of tri-*o*-tolyl phosphate or other high-boiling liquids, usually esters. By varying the amount of plasticizer used, products ranging from flexible, semihard materials through extensive (500 per cent elongation at break) rubberlike products to thermoplastic gels may be obtained.

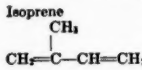
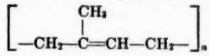
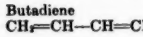
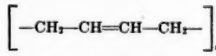
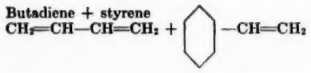
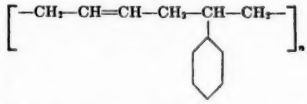
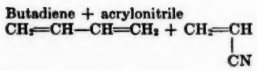
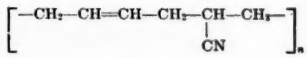
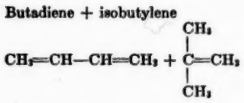
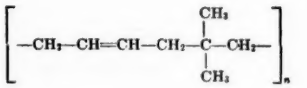
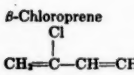
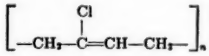
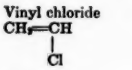
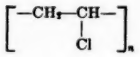
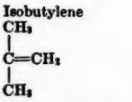
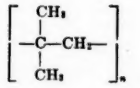
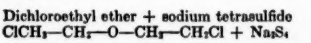
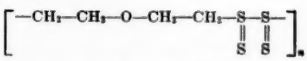
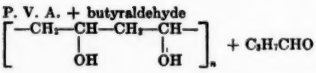
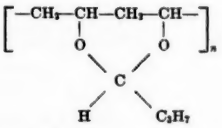
Isobutylene, a product of the cracking of petroleum, may be polymerized catalytically over boron trifluoride or other amphoteric halides to give products ranging from viscous sirups to elastic solids. Under suitable conditions the liquid monomer can be converted almost quantitatively into a rubberlike polymer. The products are sold in this country under the trade names of Vistanex and polybutene. It is rumored that isobutylene is likewise used as the principal monomer in the production of Butyl Rubber.

PROPERTIES AND APPLICATIONS

It is beyond the scope of this paper to explore in any detail the properties and applications of the various types of synthetic rubbers. Wood[29] presented a comprehensive review of the literature on this subject up to June, 1940. More recent contributions are those of Schade[19], Sebrell and Dinsmore[20], and Street

TABLE I

STRUCTURAL RELATIONS AMONG MONOMERS AND POLYMERS

Monomers	Basic recurring groups of polymers	Nature of product
Isoprene 		Natural rubber or caoutchouc
Butadiene 		Buna-85 and Buna-115 (German); no U. S. production
Butadiene + styrene 		Buna-S, Buna-SS
Butadiene + acrylonitrile 		Buna-N, Perbunan, Hycar-OR*, Chemigum*
Butadiene + isobutylene 		Butyl Rubber*
β-Chloroprene 		Neoprene
Vinyl chloride 		Koroseal, Flamenol, Vinylite-Q
Isobutylene 		Vistanex
Dichloroethyl ether + sodium tetrasulfide 		Thiokol-B
P. V. A. + butyraldehyde 		Butacite, Butvar, Vinylite-X

* Identity not disclosed by the manufacturer but reported to be of the type indicated.

and Ebert[23]. The latter two papers, in particular, present detailed compounding results and comparative data obtained in a number of topical physical tests run on the various Buna types, including Buna-S, Buna-N, Chemigum, and Hycar-OR, two grades of Neoprene, and Thiokol. The properties of the butadiene types were described by Stöcklein[22] and Koch[15]. Anderson[2], and Garner and Westhead[13] give comparative data on Neoprene and Buna types. The compounding of Butyl Rubber and the properties of its vulcanizates are described in a comprehensive paper by Thomas and associates[24]. The properties of the Polybutenes are described by Sparks and coworkers[21A], those of the Thiokols by Patrick[17], and those of Koroseal by Brous and Semon[5]. In view of this extensive literature, only broad generalizations will be discussed here.

This approach has its shortcomings, however, and it is realized that in several instances an oversimplication of the subject matter will result. For example,

Neoprene should not be treated as a single entity, because there are a number of types of polymers on the market which bear this generic name, each possessing inherently different properties and each offered for different specific applications. This same statement probably holds true, in lesser degree, for most of the other synthetic rubbers. In attempting to generalize about properties, broad statements may be made which, although valid for a given class of synthetic rubbers, may not hold for specific types. This criticism may be directed likewise at the broad comparisons of the synthetic rubbers as a group with natural rubber.

The compounding, *i.e.*, the art of selecting the kind and quantity of the various ingredients added to rubber to vulcanize it and impart to the product specific desired properties, follows, in the case of the Buna types, the same basic principles found for natural rubber. The proportion of sulfur necessary for vulcanization, is, less than that normally used with rubber in order that satisfactory elongation be maintained. The same organic accelerators have been used, although there are indications that more active and specific types will be demanded. The effect of antioxidants is not so pronounced because the synthetics themselves are quite resistant to oxidation. Of the reinforcing agents, the carbon blacks have the most effect on mechanical properties, the magnitude of the reinforcement being greater on a percentage basis than is obtained with natural rubber.

The proportions of oils and plasticizers required for satisfactory processing is far greater for the synthetics; this is one respect in which they suffer seriously in comparison. Because they are more resistant to oxidation and because they contain more cross-linked type of polymeric structure than natural rubber, they do not soften or break down so readily on milling and, hence, are more difficult to process. Pigments do not disperse in them so readily, and the unvulcanized mixes do not calender or extrude so satisfactorily. To the extent that plasticizers are added to overcome this deficiency, the physical properties of the vulcanized product are proportionately decreased.

Neoprene is unique among the butadiene-derived polymers in that its vulcanization does not depend on sulfur; that is, it may be effected simply by heating. The metallic oxides, such as magnesium and zinc oxides and litharge, function as vulcanizing agents and, strangely, sulfur when used with them acts as an accelerator. Some of the organic accelerators of vulcanization exhibit the same property in Neoprene. Many exhibit entirely different and unexpected results; *e.g.*, benzothiazyl disulfide (Altax) functions instead as an effective retarder. Others, particularly the substituted ammonium salts of the dithiocarbamic acids derived from secondary amines, exert a pronounced plasticizing action when added during milling. The reinforcing powders may increase modulus but, unlike their behavior in rubber, they do not increase the tensile strength of Neoprene vulcanizates.

The Thiokols can be made to undergo a change similar to vulcanization in spite of the fact that they are saturated. As with Neoprene, metallic oxides act as vulcanizing agents and sulfur as accelerator. In this case Altax functions as a plasticizer. Reinforcing agents, particularly carbon blacks, are required to obtain the optimum tensile strength.

Koroseal contains no double bonds and, accordingly, is not vulcanizable by the ordinary processes employed by the rubber industry. However, a novel method for the vulcanization of polyvinyl polymers to give elastic products through the use of polymerizable or vulcanizable plasticizers was recently disclosed by Garvey and coworkers[14]. This concept is so new that what its effect will be on the development on this class of polymers cannot now be foretold.

The addition of reinforcing agents to Koroseal does not increase its tensile strength, although other physical properties may be improved. Its mechanical properties depend primarily on the percentage of plasticizer added. Compositions may be prepared on an ordinary rubber mill, and processed with the machinery normally employed for rubber.

The applications of the synthetic rubbers may be classed in two main categories: simple replacements of natural rubber in its manifold uses, and special products whose specifications cannot be met by natural rubber. Each of the synthetic products possesses one or more properties in which it is superior to natural rubber or other synthetics. The individual synthetics are not so versatile in their applications or modification by compounding, but since they vary so greatly among themselves in inherent properties, a specific requirement can be met by proper selection. Whereas the rubber compounder formerly had only one elastic base material on which to build a stock to meet a given specification, he now has at his command a whole series of elastic raw materials.

The applications involving simple replacement of natural rubber have been only experimental. The day when the synthetics will be competitive on a price basis is still in the future. Furthermore there is no incentive, as long as crude rubber is available, to use them in such products as tires and tubes because the present synthetic materials are not superior in most mechanical properties. However, if the rubber industry were forced to turn to the synthetics as the sole source of supply of "rubber", it is reasonable to assume on the basis of compounding information already at hand that, with the proper additional development work, all types of "rubber" goods could be produced, and that the products would be comparable in quality with those now produced from natural rubber.

The total consumption of crude rubber in 1939 was distributed as follows: tires, 63.6 per cent; tubes, 9.2; repair materials, 3.1; mechanical goods, 9.0; drugs and sport sundries, 5.0; boots and shoes, 6.8; miscellaneous, 3.3. Extensive experimental work involving road tests, and small volume sale to the public in one case, has been done on the adaptation of synthetic rubber to tires. In Germany, where the greatest replacement in this field has taken place, Buna-S has been used almost exclusively. In this country, satisfactory tire tread stocks have been developed from all of the Buna types and from Neoprene. Butyl Rubber also should be applicable. The wear resistance of synthetic tire treads in road tests has been comparable and, under some conditions, superior. Two major difficulties in adapting the synthetics to tires remain: Unvulcanized synthetic rubber-carbon black stocks cannot be processed without excessive proportions of softeners, and the use of synthetic rubber in the carcass of the tire has not proved satisfactory because of poor adhesion.

The applications depending on some superiority of the synthetic products are at present consuming practically all of our production. For these applications the higher cost of the synthetics is offset by the superiority of some of their properties. The comparison of the superiorities of the synthetic materials, considered as a broad class, and of natural rubber may be summarized as follows:

The synthetics are superior in:

1. Resistance to deterioration by oils and organic solvents
2. Resistance to oxidation or aging
   a. Induced by actinic rays
   b. Induced by heat
   c. Induced by strong oxidizing agents
3. Lower permeability to gases

Natural rubber is superior in:

1. Processing properties
2. Extensibility and elasticity
3. Resiliency (*i.e.*, low hysteresis)
4. Resistance to stiffening at low temperatures *

The oil resistance of the Buna-N types, Hycar-OR, some types of Chemigum, Neoprene, Thiokol, and Koroseal is excellent. Exemplifying this superiority are the use of Buna-N types, Neoprene, and Thiokol in the linings of all types of hose required in the petroleum industry; Neoprene, Thiokol, and Koroseal in printing rolls and engraving plates; Koroseal in seals, gaskets, and plunger diaphragms for oil pumps; Neoprene and, more recently, plasticized polyvinyl alcohol in oil-resisting gloves.

All types of synthetic rubber are more resistant that natural rubber to normal oxidation. Neoprene, Thiokol, and Koroseal, moreover, are outstandingly resistant to the action of sunlight and other actinic rays and of ozone, conditions under which the life of natural rubber is quickly cut short. They are accordingly used in many parts of airplanes which are subject to direct sunlight. Gas-cell fabrics in balloons and airships are now coated with Neoprene and Thiokol, which, in addition to their resistance to sunlight, are far less permeable to gases than is natural rubber.

The combined resistance to oil and heat of some types is used to good advantage in mechanical goods. Numerous parts, such as motor supports, gaskets, grommets, and insulated wire made from Neoprene, Thiokol, Hycar, and Chemigum, are used in automobiles, airplanes, tanks, and ships. The consumption of synthetic rubber in this field accounts for the bulk of the current production of all types.

The synthetics are being adopted extensively for insulated wire, not because of any superiority in electrical properties (some types are inferior to rubber) but because of their better resistance to burning. Neoprene and Koroseal are outstanding in this respect, and may be used alone for low voltages or as a jacketing layer over insulation of natural rubber for higher voltages. The principal application today is in insulated wire going into warships.

Oil- and light-resistant fabrics used in raincoats and tarpaulins for the armed forces are being produced in great quantity from Neoprene and Koroseal. Another important defense use of several of the synthetics is in bullet-proof gasoline tanks. The importance of the synthetic rubbers as vital products in the defense program is indicated by the action of the Office of Production Management in placing all types under priority control in June, 1941.

ECONOMICS OF SYNTHETIC RUBBER PRODUCTION

The availability and potential supply of raw materials are of primary consideration in approaching the problem of costs. The basic raw material which will be required in the greatest tonnage is butadiene. As already indicated, petroleum by-product butane and butenes constitute our main supply of this raw material. Egloff[10] estimated recently that the petroleum industry could supply the raw material to produce butadiene and styrene at the rate of 85 billion pounds a year without lessening production of any of the other products required for peacetime or national defense needs. By comparison the estimated figure of

* Yerzley and Fraser [*Ind. Eng. Chem.*, March, 1942] describe a new type of oil resistant Neoprene (Neoprene Type-FR), the vulcanizates of which are comparable, as judged by retractability, with natural rubber in resistance to freezing.

1,650,000,000 pounds for the consumption of crude rubber in the United States in 1941 is completely dwarfed. Butane is selling currently for 3 cents per gallon or 0.6 cent per pound. It may be concluded, therefore, that we are in a fortunate position in this country with respect to a supply of cheap raw materials.

As a result of relatively small-scale production, butadiene is now being produced to sell in the range 20-25 cents, styrene at 30-35 cents, and acrylonitrile at 35 cents per pound. The cost of the various Buna types derived from these monomers is likewise high at this time, because of the relatively low tonnages being produced. It has been estimated reliably, however, that on a large tonnage basis, butadiene could be produced for 10-15 cents and the finished polymers for 20-25 cents per pound. The price of crude natural rubber is now approximately 23 cents. To be competitive with natural rubber at its present price on a volume basis, the various synthetic products would have to sell at the following prices:

	August 1941 price	Density	Equivalent price
Natural rubber	$0.23	0.92	$0.23
Neoprene Type-GN	0.65	1.24	0.17
Buna-S	0.60	0.96	0.22
Perbunan	0.70	0.96	0.22
Thiokol-F	0.45	1.38	0.15
Vistanex	0.45	0.90	0.24
Koroseal (30% plasticizer)	0.60(est.)	1.33	0.16
Hycar-OR	0.70	1.00	0.21

UNITED STATES PRODUCTION CAPACITY

The production of synthetic rubbers has been increasing steadily since 1932, but has not represented more than a fraction of one per cent of our total rubber requirements until recent years. Neoprene (originally Duprene) was the first synthetic product to be made in commercial quantities, and it has led the field in yearly production from the beginning. The estimated total production figures for the past two years and for 1941 for all types are:

1939	2,500 long tons
1940	4,000
1941	17,000

The 1941 production may be broken down as follows:

Buna types	4,000 long tons
Neoprene	6,500
Thiokol	1,500
Polyvinyl chloride types (plasticized)	5,000
Total	17,000

The current production is entirely from privately owned plants, and under normal world conditions the building of additional plants would be undertaken by private industry as improved manufacturing methods were developed and the demand for the resulting products increased. However, to undertake the building of large plants capable of producing our normal requirements in rubber (600,000 long tons per year), or even an appreciable fraction of it, would require a capitalization greater than the individual rubber companies could finance. Accordingly, as the Far Eastern situation became more threatening in early 1940, Congress began to study the advisability of building large government-financed

plants. On June 14 of that year the Senate Committee on Military Affairs held a hearing on Bill S4082 to appraise the progress made by industry in the development of synthetic rubbers, and to explore the potentialities of our building plants to produce our own rubber. In view of the action finally taken in May, 1941, by the Government, it is of interest that, in this hearing, plants were considered which would produce 100 and 300 tons per day. On an annual basis such plants would make approximately 35,000 and 100,000 tons, respectively. It was estimated that the smaller plants would cost around $10,000,000 and the larger $25,000,000 to $50,000,000, depending on the type of rubber produced. On the basis of these figures, plants large enough to supply our normal requirements of rubber would require a capitalization of $150,000,000 to $300,000,000. Any plans which may have been under consideration to build such large plants were discarded in favor of smaller units. This was fortunate, perhaps, because the erection of such plants would have tended to freeze the entire development of synthetic rubbers at the pilot-plant stage.

In May, 1941, Jesse Jones announced the Government's decision to build four government-owned synthetic rubber plants. Each plant will have an initial production capacity of 10,000 tons per year* and will be operated under a lease agreement by the four major rubber companies, The B. F. Goodrich Company, The Goodyear Tire & Rubber Company, The Firestone Tire & Rubber Company in Akron, Ohio, and the United States Rubber Company at Naugatuck, Conn.

The plants for producing the other types are also being expanded rapidly. Du Pont is increasing the capacity of its Deepwater, N. J., plant from 6000 to 9000 long tons per year, and is building a new plant at Louisville, Ky., the capacity of which will be 10,000 long tons. These plants are expected to be in production by early 1942. Thiokol Corporation announced in May the completion of a new unit at the Dow Chemical Company's plant in Midland, Mich., bringing their total capacity up to 330,000 pounds per month or 1750 long tons per year. Plans were disclosed at the same time for another unit which will increase the present capacity by 50 per cent. The B. F. Goodrich Company has expanded its Koroseal plant at Niagara Falls; when its new plant at Louisville is completed, its current production of Koroseal will be quadrupled. Although no production data have been given out on this product, it has been reported that the total production of polyvinyl chloride polymers, *i.e.*, including the Vinylites as well as Koroseal, runs at present at about 3575 long tons per year and that, after the second quarter of 1942, it will be increased to 11,000 long tons. These figures are for the unplasticized material. The percentage of plasticizer normally added runs between 30 and 40 per cent.

The above data for present and projected production of synthetic rubber are summarized as follows (in long tons):

	July 1941	January 1942	January 1943
Buna types	5,000	10,750	70,000
Neoprene	6,500	9,000	19,000
Thiokol	1,750	1,750	2,650
Polyvinyl chloride (40% plasticizer)	5,000	6,000	18,000
Total	18,250	27,500	109,650
% of normal requirements	3	4.6	18.2

* On January 12, 1942, Jesse Jones announced a further expansion of the synthetic rubber program costing $400,000,000, which will provide for the manufacture of 400,000 tons per year in addition to the production of plants already in operation or under construction. At the same time it was disclosed that the national stock pile of natural rubber was 600,000 tons.

Obviously, a production capacity of 18 per cent of our normal requirements would leave us in a serious condition if our supply of crude rubber from the Far East was cut off for any extended period. In such an event the building of the larger plants already discussed would undoubtedly be undertaken. However, authorities in the rubber industry estimate that a minimum of three years would be required to build these superplants. To bridge the gap until they could be completed, the Reconstruction Finance Corporation has allotted the funds required to accumulate a reserve stock pile of 515,000 long tons of crude rubber, or a 10-month supply. At present the accumulation in this government reserve is about 225,000 tons. Our total stock, including this reserve, the stocks in company warehouses, and those afloat, is equivalent to a 9-month supply. In the effort further to conserve what supplies we have, the Government, through the Office of Production Management, has issued a general priority order to curtail the consumption of rubber for the balance of 1941 under a quota system. The Government likewise has taken over the importing of all rubber into this country and has established a price ceiling on it*.

Conservation is being accomplished also by extending the supply at hand through the use of increased quantities of reclaimed rubber. We shall probably use 200,000 tons of this commodity this year. Fortunately our supply of scrap rubber is more than ample.

The consuming public likewise has the opportunity to aid in conservation by observing those precautions necessary to obtain the maximum service from rubber goods. Programs and drives to educate the public in ways to minimize road wear of tires are now being undertaken throughout the country.

CONCLUSION

We may survey with some satisfaction the progress made in the development of synthetic rubber in the United States during the last decade. In this period four new types of synthetic elastic polymers have been developed: Neoprene, Thiokol, Koroseal, and Butyl Rubber. Extensive knowledge of the chemistry and engineering involved in the production of a large variety of types has been acquired. The plants in operation and under construction for the manufacture of these varied types are rapidly approaching such capacity as to justify the use of the expression "synthetic rubber industry". True, it is an infant industry hardly out of the pilot-plant stage and far from ready to relieve the coolie in the Far East of his job; but it is growing rapidly, fed by a more than ample supply of cheap raw materials, and has already taken an important role in the defense program as a producer of vital war materials. Its growth is being stimulated at present by the emergency now facing the country, but it may be expected to continue to expand after the emergency is over because the synthetic rubbers as a group are outstandingly superior to natural rubber under certain severe service conditions.

ACKNOWLEDGMENT

The writer wishes to thank R. F. Dunbrook of The Firestone Tire & Rubber Company for his collaboration in the preparation of this paper.

* In December, 1941, the Government imposed additional stringent restrictions on the use of rubber in order to minimize the effects of the Far Eastern war. The Office of Production Management, in General Preference Order M-15-b, restricted the use of rubber to fill orders assigned an A-3 or better preference rating and to the manufacture of twelve other specific classes of articles judged to be essential. At the same time the sale of all rubber tires other than bicycle tires, except to fill order assigned an A-3 or better preference rating, was prohibited until January 5, 1942, when such sale to the public was placed on a strict rationing basis.

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BRITTLE POINT OF RUBBER ON FREEZING *

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The need for a simple method of determining brittle points which would be adaptable to a large number of materials led the writers to develop the apparatus described below. There is presented here, for the first time, brittle point data on certain natural and synthetic rubber compositions.

The study of the variation with temperature of the mechanical properties of elastomers is of immediate practical and theoretical interest. Recently Kistler[11] attempted a correlation of temperature-strength data of polymers with their chemical structure. On the other hand, the increasing use of synthetic high polymers at low temperatures for insulation and mechanical purposes requires a more complete knowledge of their behavior under conditions of extreme cold[2, 14, 16, 17].

The determination of the brittle point offers a simple method for investigating the possible use of a new material at low temperatures. In 1928 Kohman and Peek[13] described a method whereby a small strip of material at a known temperature was bent quickly through 90° by a hammer blow. They found that within rather wide limits the brittle temperature was independent of the sample dimensions and bending angle, but that a high rate of deformation was necessary for reproducible results. The brittle point was found to be definite and reproducible within ±2° C for the materials studied. Using this method, Kemp[10] determined the brittle point range of crude and vulcanized rubber, balata, guttapercha, and paragutta.

In 1938 the I. G. Farbenindustrie[9] advocated a test in which, at the brittle point, a falling weight would break a strip of the material bent double on a flat surface. Six samples could be tested at once. No brittle points were given. This method is limited to materials which can be so bent without breaking.

Recently Koch[12] determined the brittle point of several elastomers by measuring the bending stress. The measuring foot of a micrometer is placed on the center of a specimen, whose ends are supported. Determination of the distortion-temperature curve allows the elastic modulus to be calculated, as well as the brittle point. The apparatus must be calibrated before use but, once calibrated, it offers a simple way of obtaining valuable data. The brittle points given by Koch agree well with those presented here, with the exception of a value of −67° C, which he gave for an unspecified rubber composition.

The elastic properties of rubber at the brittle point were mentioned by Whitby[19] in a discussion of the "elasticity temperature", while Houwink[8] used the term "high elasticity temperature" for the brittle point. Bekkedahl[1], and Wood, Bekkedahl, and Peters[20] showed that crude rubber exhibits a transition of the second order around −70° C. A large change in the coefficient of expansion is noted at this point. Vulcanized rubber undergoes the transition ap-

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proximately 10° C higher for each 2 per cent of combined sulfur from −72° C (2 per cent sulfur) to −53° C (6 per cent sulfur).

Ferry and Parks[8] found a similar transition at about −73° C for polyisobutylene of molecular weight 4900. These transition points are characteristic of the softening behavior of truly amorphous materials, such as glass[5].

Changes in the slope of volume-temperature curves are also used by Ueberreiter[18] to find transition points for a wide variety of plastics He links these points with sharp changes in the relaxation time of the molecule with changing temperature.

Investigation of the brittle point of polystyrene and polyvinyl chloride has become important because their brittle points of 80° and 81° C, respectively, are above room temperature[18]. In this case the plasticizer, which markedly changes the brittle point, becomes of great interest. The mechanism of plasticizer

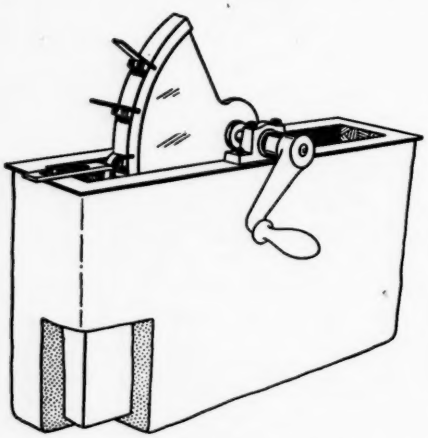

Fig. 1.—Simple brittle point Apparatus.

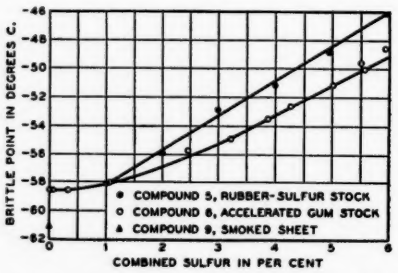

Fig. 2.—Brittle point *vs.* combined sulfur for compounds 5, 6, and 9.

action was recently discussed by Gloor and Gilbert[7]. Russell[15] determined the brittle temperature of various plasticized polyvinyl chloride compounds by finding the temperature at which a sample bar shattered when bent double.

Fuoss[4] discussed in detail the interpretation of the brittle temperature. He showed that the mechanical, electrical, and thermal properties of polyvinyl chloride are very different above and below this point. An analogy with liquids is proposed, which characterizes the brittle point as an internal melting point.

No exact correspondence seems to exist between these second-order transition points and brittle points in the case of rubber and polyisobutylene. In both cases the brittle temperature is several degrees higher than the transition temperature. This is understandable, since the brittle point as defined by experiment is to some extent arbitrary.

APPARATUS

The apparatus for brittle point determination shown in Figure 1 consists of an insulated steel tank, 14×2×8 inches (35.56×5.08×20.32 cm.) at the top center of which is mounted a brass quadrant of 4.87-inch (12.37-cm.) radius, keyed to a shaft. Six notches, 0.25 inch (6.35 mm.) deep and 0.075 inch (1.905

mm.) wide, are spaced at 2-inch (5.08-cm.) intervals on the rim of the quadrant. Each notch is backed with a block extending 0.25 inch above the rim. A rigid arm, 0.125 inch (3.175 mm.) thick with a rounded end, is mounted in the side of the tank extending to within 0.5 inch (1.27 cm.) of the rim of the quadrant. The shaft upon which the sample-holding fixture is mounted has a crank which, on rotation, immerses the specimens in the tank.

After coming to temperature in the bath liquid, the specimens are brought sharply in contact with the rigid arm by rapid rotation of the crank.

Acetone is used as the bath liquid, with solid carbon dioxide added directly as the refrigerant. For lower temperatures down to −120° C, methylcyclohexane and liquid nitrogen are recommended. A stirrer placed in one end of the tank provides agitation. The temperature is measured with a partial immersion toluene thermometer reading −100° to +30° C and graduated in 1° C. The insulation of the tank is such that at −60° C the temperature rise is 1° C in 3 minutes, the rates decreasing with increasing temperature. This makes it possible to break samples at a given temperature, insert fresh strips, and repeat the trial 1° C higher without having to add solid carbon dioxide. A 300-watt immersion heater was used to raise the temperature of the bath rapidly when desired. The entire apparatus should be placed in a hood.

DETERMINATION OF BRITTLE POINT

The material to be tested is most conveniently moulded into a 0.075-inch (1.905-mm.) sheet. Strips 1.5×0.5 inch (3.81×1.27 cm.) are cut from this sheet. If desired, several strips may be tested at one time. In the work described here, only one strip was tested at a time. This was necessary for accurate readings, since many rubber compounds become stiff and tough near the brittle point, and it is thus impossible to rotate the crank with sufficient speed to break more than one strip at a time and still maintain the necessary high rate of deformation[13]. To locate the point approximately for comparison purposes or for materials less tough than rubber, multiple tests are useful. If the sample was thicker than 0.075 inch, it was trimmed to fit the notch; if less than the required thickness, strips of paper wound around the end served to wedge it in place. The clearance between the notch block and the projecting arm was 0.25 inch. This proved satisfactory for samples 0.050 to 0.100 inch (1.27 to 2.54 mm.) thick. It was found that specimens under 0.050 inch gave low brittleness values, because the strip was not rigid enough to bend at only one place during the test. If the clearance was reduced to 0.125 inch, samples only 0.025 inch could be tested; 0.005-inch films gave good results with a 0.031-inch (0.787-mm.) clearance. Samples beyond 0.100 inch thick offer difficulty in breaking.

Most materials break off cleanly and completely at the brittle point. Highly loaded natural or synthetic rubber compounds show a range of 3-4° C over which the extent of fracture increases before break is complete at the low end of the range.

The thermometer used was calibrated to 0.1° C every 10°. The error due to imperfect immersion to the mark was about ±0.1° C. The reproducibility of the brittle point from samples of the same sheet was about ±0.1° C. The approximate brittle point of an unknown or new material is located first by testing samples every 10° C, starting from −70°. Then fresh samples are broken every 1° until, for example, at −50° C the sample breaks while at

$-49°$ it remains undamaged. This is then checked by lowering the temperature to $-52°$ and testing a new strip every degree to $-47°$. The brittle point is then taken as between the two temperatures; in this case $-49.5° \pm 0.5°$ C.

In special cases, such as for the compounds listed in Table I, where the brittle point is desired within $\pm 0.1°$ C, strips are tested at 0.1° C intervals between the two temperatures determined above. The brittle point is best determined 24 hours or more after preparation of a compound. This is the recommended procedure for the other physical tests which are usual on rubber compounds.

The brittle points of liquid materials may be found by casting test strips in small metal foil molds, freezing in solid carbon dioxide or liquid air, and testing as usual. The foil does not affect the test. This was the procedure with melted rubber and low-molecular-weight polyisobutylene.

TABLE I

BRITTLE POINT AND STATE OF CURE

Compound	Cure		Brittle point (° C) (± 0.1°)	Parts combined sulfur/100 parts rubber
	Temp. (° C)	Time (min.)		
1. Gum stock (100 smoked sheet, 0.5 mercaptobenzothiazole, 6.0 zinc oxide, 0.5 stearic acid, 3.5 sulfur)	126	20	—59.3	—
		30	—59.2	—
		40	—59.2	—
		80	—59.1	—
		120	—57.9	—
2. Gum stock (100 smoked sheet, 3.0 tetramethylthiuram disulfide, 5.0 zinc oxide, 0.5 stearic acid)	142	15	—59.7	—
		30	—59.6	—
		45	—59.9	—
		60	—59.9	—
3. Polychloroprene gum stock with 15 parts carbon black	142	15	—39.2	—
		30	—39.6	—
		45	—39.7	—
		60	—39.6	—
4. Rubber-sulfur stock (100 smoked sheet, 10 sulfur)	148	60	—56.5	—
		120	—50.5	—
		180	—44.0	—
		240	—39.5	—
5. Rubber-sulfur stock (100 smoked sheet)				
+ 1 sulfur	148	720	—58.1	1.00
+ 2 sulfur		720	—55.9	2.00
+ 3 sulfur		720	—52.9	3.00
+ 4 sulfur		720	—51.2	4.00
+ 5 sulfur		720	—48.9	4.98
+ 6 sulfur		720	—46.1	5.99
6. Gum stock (100 smoked sheet, 0.5 benzothiazyl disulfide, 2.0 phenyl-α-naphthylamine, 6.0 zinc oxide, 0.5 stearic acid, 6.0 sulfur)	142	0	—58.6	0.00
		5	—58.6	0.07
		10	—58.6	0.33
		20	—58.0	1.05
		40	—55.7	2.46
		60	—54.9	3.24
		90	—53.5	3.86
		120	—52.6	4.27
		180	—51.2	5.01
		240	—49.6	5.52
		360	—50.0	5.58
		720	—48.6	5.97

BRITTLE POINT AND STATE OF CURE

The data in Table I under compounds 1 and 2 show that the brittle point of soft vulcanized rubber is substantially independent of the state of cure within the curing limits found in industrial practice. The polychloroprene compound studied in this connection (compound 3) shows the same behavior.

In the case of rubber-sulfur compounds, and in other cases where a large amount of sulfur is used, the brittle point varies nearly linearly with the amount of combined sulfur. This is brought out in Figure 2, where the data for compounds 5 and 6 are plotted. The extended linear portions of both curves intersect the temperature axis near the brittle point of rubber itself, *i.e.*, −61.5° C. Once the curve, as given above, was known for a compound of this type, the determination of the brittle point could be used as a measure of the coefficient of vulcanization, which in many cases would uniquely determine the state of cure. This would be analogous to the T-50 type of test.

RUBBER AND COMPOUNDS

The brittle points of various types of crude rubber and rubber stocks are given in Table II. Smoked sheet rubber which had been cooled quickly in a solid carbon dioxide-acetone bath remained transparent and unchanged in

TABLE II

BRITTLE POINT OF GUTTA-PERCHA, RUBBER, AND COMPOUNDS

Compound	Cure		Brittle point (° C ± 0.5°)
	Temp. (° C)	Time (min.)	
7. White gutta, first-grade Tjipetir	109	5	−53.5
8. Whole-latex rubber, ammonia-preserved, air-dried	—	—	−61.5
9. Smoked sheet rubber	116	30	−60.7 to −61.5
10. Brazilian fine para, unmilled	—	—	−58.5
11. Smoked sheet, milled 6–30 minutes	109	5	−61.5
12. Plantation-softened smoked sheet	135	20	−60.5
13. Pale crepe rubber	109	60	−62.5
14. Pale crepe rubber heated at 202° C (mol. wt. 6000)	—	—	−48
15. Gum stock	148	80	−59.5
+ 10 parts medium oil	—	—	−58.5
+ 30 parts mineral rubber 265° F	—	—	−55.5
+ 30 parts mineral rubber 310–325° F	—	—	−54.5
16. Gum stock	—	—	—
+ 20 parts channel black	135	60	−57.5
+ 40 parts channel black	—	—	−56.5
17. Gum stock	—	—	—
+ 100 parts zinc oxide	—	—	−60
+ 200 parts zinc oxide	—	—	−59.5
+ 300 parts zinc oxide	—	—	−58.5
18. Gum stock	135	8	−53.2
+ 27.6 parts $CaCO_3$	—	—	−48.5
+ 55.2 parts $CaCO_3$	—	—	−41.5 to −53.5
19. Tube reclaim	—	—	−52.5
+ 5.25 parts sulfur	142	25	−50.5
20. Tire carcass reclaim	—	—	−50.5
+ 5.25 parts sulfur	142	17	−46.5
21. Tire tread reclaim	—	—	−49.8
+ 5.25 parts sulfur	142	17	−48.5
22. Shoe stock reclaim	—	—	−44.5
+ 5.25 parts sulfur	135	30	−42.5

appearance. This amorphous rubber had a brittle point of −61.5° C. Specimens from the same sheet were frozen 2 weeks at −5° C. The crystallized specimens were opaque and stiff, with a brittle point of −59.5° C. Additional samples

TABLE III

BRITTLE POINT OF SYNTHETIC ELASTOMERS

Compound	Cure		Brittle point (° C ± 0.5°)
	Temp. (° C)	Time (min.)	
Polychloroprene [a]			
23. Milled 5 minutes	109	10	−36.8
24. Gum stock	142	30	−38.5
25. + 3 parts soft black + 8 parts oil	142	20	−40.6
26. Gum stock + 5 parts channel black + 20 parts oil	142	30	−42.5
27. Gum stock + 100 parts soft black + 8 parts oil	142	30	−36.4
28. Gum stock + 200 parts soft black + 10 parts oil	142	30	−32.0
Butadiene polymer			
29. Milled 5 minutes	135	10	−67.8
30. Gum stock [b]	148	60	−65.5
31. Tire tread stock [c]	148	60	−71 to −69
Butadiene-styrene copolymer			
32. Milled 2 minutes	153	30	−65.5
33. Gum stock	148	60	−65.5
34. Tire tread stock	148	60	−66 to −70
Butadiene-acrylonitrile copolymer			
35. American	—	—	−49 to −52
36. German	148	15	−45.5
37. Gum stock	142	45	−42 to −45
38. Tire tread stock	142	45	−46.5
Butadiene-nitrile copolymer, type I			
39. Milled 5 minutes	148	10	−25.6
40. Gum stock	153	45	−24.5
41. Clay-loaded stock	153	45	−29.0
42. Soft stock (dibutyl phthalate, 50 parts)	153	45	−42.5
Butadiene-nitrile copolymer, type II			
43. Milled 1 minute	—	—	−29.3
44. Gum stock	153	45	−29.5
45. Tire tread stock	153	30	−26 to −28
Organic polysulfide			
46. Type I	—	—	+ 7.0
47. Type I, carbon black stock	142	50	− 3.8
48. Type II, carbon black stock	148	30	−22.5
49. Type III	—	—	−35.3
50. Type III, carbon black stock	148	50	−34.0
51. Type IV	—	—	−35.5
52. Type IV, carbon black stock	142	50	−39.5

[a] Polychloroprene having improved freeze resistance was recently made commercially available. This material gives products with brittle points 8–12° C lower than the values given in Table III for regular polychloroprene.

[b] All compounds listed as gum stock in Table III, except 24, had the following composition: 100 synthetic elastomer, 1 benzothiazyl disulfide, 5 zinc oxide, 1 stearic acid, 5 Cumar resin, 1 sulfur.

[c] All compounds listed as tire tread stock had the same composition as the corresponding gum stock, with the addition of 50 parts of channel black.

were heated to 120° C in air for 1 hour to melt all crystals. They broke at −61.5° C. This experiment thus failed to demonstrate any large difference in brittle point of the more crystalline "frozen" rubber and the ordinary amorphous type.

Smoked sheet milled for 6 to 30 minutes on cold mill rolls and broken down to the maximum amount possible (about 30,000 molecular weight) still has the same brittle point. However, rubber which has been heated in tetralin at 202° C for 11 hours, and broken down to a molecular weight of about 6000, has a brittle point of −48° C. Gee and Treloar[6] reported the "low temperature limit of elastic extensibility" of rubber fractions of molecular weight 63,000-360,000 to be nearly constant at about −68° C: "The low temperature limit of elastic extensibility was determined by cooling the specimen to below −70° C, and then allowing the temperature to rise slowly until an extension of 100 per cent was produced by a weight of one kilogram." It would thus appear that, between the molecular weights of 6000 and 30,000, the elastic properties of rubber undergo a considerable change. The same phenomenon is described below in the case of polyisobutylene.

All of the rubber compositions listed in Table II have brittle points above that of crude rubber. That the brittle point can be lowered is shown by the following experiments: 15 parts of dipentene were milled into 100 parts of smoked sheet. The resulting tacky mix had a brittle point of −70° C. A pure

TABLE IV

EFFECT OF MOLECULAR WEIGHT ON BRITTLE POINT

Material	Approx. wt. mol.	Appearance	Brittle point (° C ± 0.5°)
53. Polyisobutylene	1,500	Viscous liquid	−23
54. Polyisobutylene	10,000	Very viscous liquid-solid....	−50.2
55. Polyisobutylene	100,000	Elastic solid	−50.2
56. Polyisobutylene	200,000	Elastic solid	−50.2
57. Polyethylene	Low	Soft, waxy	−15
58. Polyethylene	High	Tough, waxy but hard.....	−68.5

gum stock using 15 parts of dipentene had a brittle point of −63.5° C. Any addition of mineral rubber or oil to natural rubber raises its brittle point. The reinforcing fillers such as zinc oxide and carbon black can be added in comparatively large quantities with only a small effect. But the use of appreciable amounts of nonreinforcing fillers such as calcium carbonate produces stocks with high brittle points. Of all the different types of reclaim, the tube type has the lowest breaking point, as would be expected.

SYNTHETIC ELASTOMERS

Contrary to the behavior of rubber, most of the synthetic elastomers have higher brittle points than their tire tread stocks. Only butadiene polymer and butadiene-styrene copolymer have lower brittle points than rubber. Garvey, Juve, and Sauser[5] reported brittleness values for a series of butadiene-nitrile copolymer compounds. Compounds 40, 41, and 42 are their stocks H, F, and E, respectively. They reported a brittle point of −55° C for the above stocks, which is not in agreement with the results given in Table III. A description of the method used by Garvey *et al.* for determination of the brittle point was not given, and probably differs from that of the authors.

Table IV gives brittle point data on polyisobutylene and polyethylene. The most striking feature of the values for polyisobutylene is that a change of average molecular weight from 10,000 to 100,000 does not change the brittle point, whereas in the range 1500 to 10,000 the brittle point drops 28° C. This is the same phenomenon shown by rubber, which on milling can be reduced to a

molecular weight in the neighborhood of 30,000 with no change in the brittle point. This would point to a certain critical range of degree of polymerization, in which the length of the chain is not great enough for full development of elastic properties in the polymer molecule.

Polyethylene of high molecular weight similarly shows a great difference in brittle point from the low-molecular-weight polymer.

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CRYSTALLIZATION PHENOMENA IN RAW RUBBER *

L. R. G. TRELOAR

In an earlier paper[1] the author has shown that plastic flow in raw rubber does not, in general, increase continuously with increasing extension but, after rising to a maximum at an intermediate extension, falls again as the extension is further increased. In the region of extension corresponding to the position of this maximum, there is a change in the nature of the recovery phenomena. Below the maximum recovery is gradual, and increases with each successive increase of temperature; beyond it, almost complete retraction takes place within a very narrow range of temperature. These and other associated phenomena were interpreted as manifestations of a change from the amorphous to the crystalline state of rubber, a change which has already been demonstrated by x-ray diffraction experiments[2].

The aim of the present experiments was to determine more precisely the relative amounts of the crystalline phase in raw rubber under various conditions of extension. For this purpose, measurements of double refraction were carried out at various temperatures under conditions of extension similar to those used in the mechanical tests previously described[1], and the changes in density which accompany the extension at a particular temperature (0° C) were investigated. Taken together, these methods have enabled a reasonably complete picture of the development of crystallization under various conditions of extension and temperature to be obtained.

THE MEASUREMENT OF BIREFRINGENCE

When stretched, a strip of rubber acquires the optical properties of a uniaxial crystal, the direction of the extension corresponding to the optic axis. Monochromatic light polarized in a plane making an angle of 45° with the optic axis is decomposed on passing normally through the strip into two components, polarized in planes parallel and perpendicular to the axis, respectively, and differing in phase by an amount δ. The birefringence may conveniently be represented as the optical path difference in wave lengths of light per mm. of thickness of the rubber. Denoting this quantity by B, the thickness of the rubber by t and the wave length of the light *in vacuo* in mm. by λ, the difference of the two principal refractive indices of the material is given by the relation:

$$n_1 - n_2 = B\lambda = \lambda\delta/2\pi t$$

The rubber films used in the optical experiments were prepared from a viscous solution of crepe in benzene by evaporation from a free drop floating on a mercury surface. By controlling the rate of drying, the resultant films were obtained perfectly flat and of uniform thickness, and, so far as could be judged, entirely free from internal strain. The dried films (thickness 0.1 to 0.2 mm.), after removal from the mercury, were washed with sodium stearate solution. This was found to prevent self-adhesion during handling, without reducing the optical transparency.

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The specimens used had a length of 20 mm. between clamps, and a width of 5 mm. Light polarized at an angle of 45° to the direction of stretch passed normally through the specimen, which was observed through a low-power microscope provided with a Babinet compensator and analyzing Nicol prism[3].

With instantaneous stretching, it was not possible to use monochromatic light, because the passage of the interference fringes across the eyepiece during the extension could not be followed. White light was therefore used. This involved some difficulty, owing to the dependence of the birefringence on wave length, which caused a spurious shift of the central black band. This effect was studied in a preliminary experiment, in which the stretching was carried out slowly, the displacement of the central fringe when sodium light was used being compared with the displacement of the fringe system in white light. Both vulcanized and raw rubber were examined, and found to give the same characteristic effects. With white light, the central black band became spread out into a spectrum as its displacement increased, and the first-order colored fringes began to merge together. When the shift in sodium light amounted to 6 fringes, the dark band in white light had apparently been displaced by an amount equivalent to 7 fringes. With further extension, this series of changes began to repeat itself.

With this preliminary experience, it was possible, in the instantaneous stretching experiments, to assign the true displacement (which was not more than 9 fringes) corresponding to the observed displacement of the central band. In calculating the optical path difference per mm. for a particular extension, the strained thickness of the rubber was assumed to be $t_0(l_0/l)^{\frac{1}{2}}$, where l_0 and l are the original and extended lengths, respectively, and t_0 the original thickness; t_0 was obtained by weighing, using the measured value of density for the rubber.

BIREFRINGENCE AT 0° C

In carrying out the experiments at 0° C[4], the specimen, mounted on a metal frame, was supported in a glass tube, closed at its lower end and immersed in a water-ice mixture in a cylindrical Dewar vessel which acted as a thermostat. The Dewar vessel was provided with two unsilvered strips along its length to permit passage of light and observation of the specimen. Each specimen was stretched instantaneously by means of a falling weight, after which the movable clamp was fixed in position, and the stretching apparatus removed. The temperature of the bath was maintained at 0° C by removing the apparatus to the refrigerator between readings.

The experimental data thus obtained are given in Figure 1. At high elongations the birefringence is seen to reach a high value immediately after stretching and thereafter to change only slightly but, at the lower elongations, the approach to the saturation value is very much slower. Evidently the rate of crystallization varies enormously with the extension, the final state being approached in a fraction of a second at the highest extension, but requiring 100 hours or more at the lowest extension employed.

Appearance of Fringes

During the observations, marked variations in intensity and uniformity of the interference fringes were noticed. At the higher extensions the fringes were uniform and clear. At an intermediate extension (325 per cent), the fringes were weak and irregular in the early stages, but gradually became clearer and more uniform as crystallization progressed. At low extensions, the phenomena were

again different. Thus, at 70 per cent extension, the fringes were clear and regular at first, *i.e.*, before appreciable crystallization had occurred, but became very faint and irregular after 7 hours. After 50 hours they increased in intensity, but continued to be rather irregular for the rest of the time. At 34 per cent extension the fringes were clear at first, but became fainter as crystallization progressed. After 25 hours they had become invisible, and readings could not be taken until 90 hours from the start, when they reappeared, and became fairly clear by the end of the experiment. An attempt was made to work at 20 per cent extension, but the fringes finally disappeared after 80 hours, and did not reappear.

To account for these changes, two effects have to be considered. They are: (1) patchy crystallization, causing irregularities in the fringes, particularly in the region of incomplete crystallization, and (2) disorientation of crystal axes discussed later, leading to scattering of light at the lower extensions.

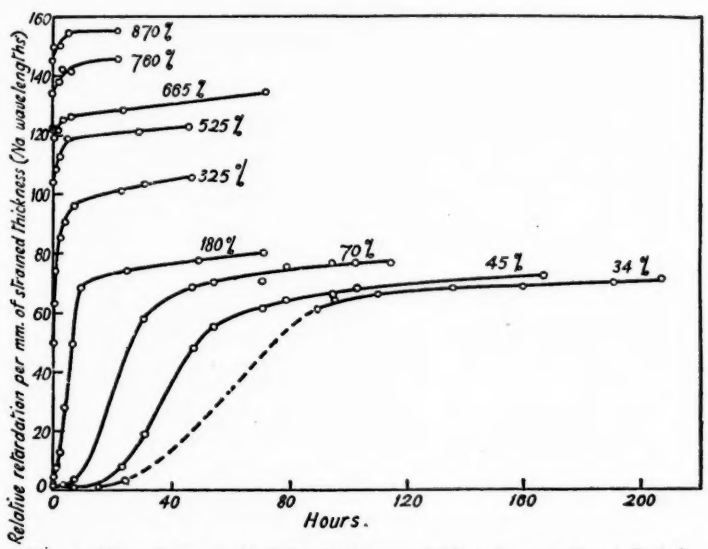

FIG. 1.—Time changes in birefringence in crepe held at the extensions indicated at 0° C.

THE BIREFRINGENCE-ELONGATION RELATIONSHIP

When the saturation values of birefringence are plotted against elongation (Figure 2, curve *c*), the points are seen to fall nearly on a straight line. This line, however, does not pass through the origin. This fact is rather surprising because, in unstretched rubber, the crystals have no preferred orientation. The birefringence must therefore become zero at zero elongation, *i.e.*, the birefringence-elongation curve must pass through the origin.

In attempting to understand how this apparent discrepancy arises, the assumption will be made that the birefringence at any elongation is determined by two factors: (1) the total amount of crystalline material, and (2) the orientation of the crystallites. Now it is known from the work of Bekkedahl[5] that rubber increases in density by about 2.65 per cent when crystallized by freezing in the unextended state. It is therefore possible, by studying density changes, to estimate the amount of crystallization directly, and thus to eliminate the effect of orientation. Experiments on these lines will now be considered.

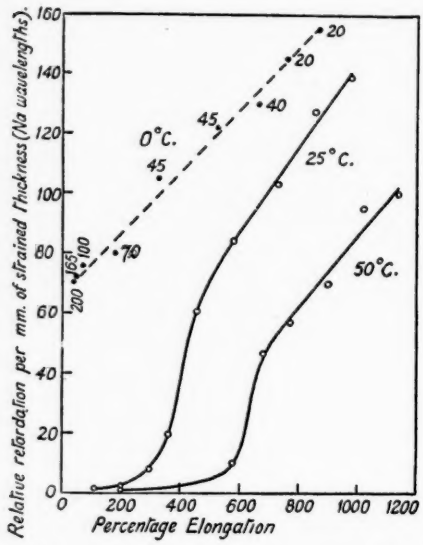

FIG. 2.—Relation between birefringence and elongation of crepe.
25° and 50° after 1 hour; 0° after hours indicated.

DENSITY CHANGES AT 0° C

Preliminary experiments were carried out with smooth-rolled smoked sheet. This was subsequently not used, because it was found by visual observations that neighboring portions of the sheet crystallized at widely different rates. The reason for these differences was not investigated, but the experiments revealed the importance of working with a material which was originally homogeneous. Further work was, therefore, carried out with a 2-mm. sheet of crepe prepared by evaporation of a solution. For this purpose a 7 per cent solution of rubber in benzene + 4 per cent alcohol was poured onto the surface of mercury, using a paper edging to allow of free contraction during drying. The sheet thus prepared was of uniform thickness and free from air bubbles. The crepe was taken from the same batch of rubber as that used in the optical experiments.

For the zero-extension experiment, a piece of the sheet was hung in a tube in a Dewar vessel containing ice-cold water. The specimen was quickly transferred to a beaker of water at 0° C, when it was required to measure the density, after which it was replaced. Readings were taken over a period of 3 weeks. For the experiments involving the application of an extension, parallel marked strips cut from the sheet were gripped between clamps in a bath of ice-cold water. Stretching was carried out by quickly pulling by hand on a wire attached to the movable clamp, after which the stretched strip (still at 0° C) was firmly clamped down to a stout board at each end, and at three other points along its length. This arrangement enabled four separate specimens to be removed subsequently at intervals for density measurements. The rubber strip mounted on the board was kept in the intervals between measurements in a lagged box in the refrigerator. The temperature registered on a thermometer placed alongside the rubber varied between 0° and −3° C during the course of the experiments; the temperature control was, thus, not so good as in the optical experiments.

The density was measured by weighing the rubber in air and in water at 0° C, the rubber being supported in a light frame of copper wire hung from the arm of the balance. Actually the temperature of measurement differed from 0° C by a fraction of a degree, and the data were corrected for the variation in density of the water and of the rubber on this account. For this purpose, the coefficient of expansion of the rubber was taken as 67×10^{-5} per degree[6]. The accuracy of the determination was limited chiefly by the quantity of rubber used. This varied from 0.27 gram at the highest to 1.0 gram at the lowest extension. At the highest extension, the errors of measurement were believed to be within 0.1 per cent. The results of these measurements are given in Figure 3, which shows the variation of density with time for a number of extensions.

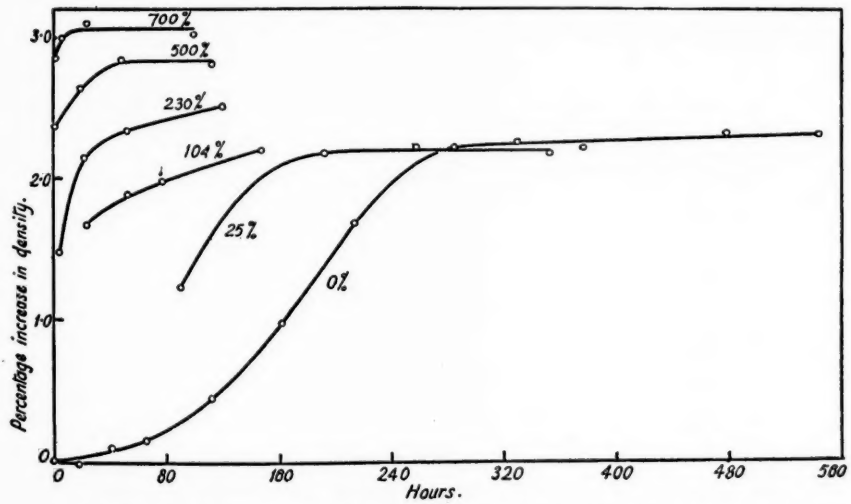

FIG. 3.—Time changes in density in crepe held at the extensions indicated at 0° C.

INTERPRETATION OF BIREFRINGENCE AND DENSITY DATA

The general similarity between the curves representing the changes in birefringence at various elongations and those representing the changes in density is at once evident. Both the rate of increase of density and its saturation value show a marked dependence on elongation. If the birefringence, like the density, depended solely on the total amount of crystalline material, then the ratio of the birefringence B to the change of density $\Delta\rho$ would remain constant as the elongation varied. Any departures from constancy of this ratio may be taken as indicative of the effect of the orientation factor on birefringence. The values of the ratio $B/\Delta\rho$ for five different extensions are set out in the accompanying table. For the first four extensions, the values of B were obtained by interpolation between the experimental curves of Figure 1, for the lowest extension, the values of $\Delta\rho$ (Fig. 3) were interpolated. The figures for the final states of crystallization, which are of chief interest, are in a separate column, in which also the data for the highest extension have been corrected to take account of the contraction of length (amounting to about 4 per cent) which occurred on cutting this specimen from the board. The optical experiments showed that with an extension of 700 per cent, this contraction on releasing the tension was accompanied by a reduc-

tion of birefringence of 5.6 per cent. This amount was therefore subtracted from B, so the figures for B and for $\Delta\rho$ should both relate to the same state of the rubber. For the remaining extensions, there was either a negligibly small contraction or a slight increase in length, so no correction was necessary.

In considering the figures in the last column of Table I, it is necessary to bear in mind the rather large experimental errors involved. It is difficult, to estimate these exactly, but it is thought that the probable error in $B/\Delta\rho$ may be as much as ± 5 per cent. From 104 to 700 per cent elongation, the final variations in $B/\Delta\rho$ are seen to be only slightly outside the limits of experimental error, though there is an indication of a slight increase in this quantity with increasing extension. Only at the lowest extension (34 per cent), was a definitely different value of $B/\Delta\rho$ obtained, but even here it was only 20 per cent lower than at the highest extension employed. The $B/\Delta\rho$ values corresponding to the shorter times, when crystalliza-

TABLE I

VARIATIONS IN THE RATIO OF BIREFRINGENCE TO CHANGE OF DENSITY UNDER DIFFERENT CONDITIONS OF EXTENSION

Elongation (percentage)	Time (hours)	$B/\Delta\rho$	$B/\Delta\rho$ (final)
700	1.3	44.5	—
700	6	44.0	—
700	22	43.9	41.4 *
500	1.2	43.0	—
500	20	44.5	—
500	72	43.4	43.4
230	3.5	33.1	—
230	22	38.6	—
230	72	37.6	37.6
104	24	31.7	—
104	52	38.4	—
104	115	37.6	37.6
34	89	46.3	—
34	207	32.3	32.3

* Corrected.

tion was still not completed, show a greater variation. Part of this variation is probably due to slight differences in the conditions in the two sets of experiments, *e.g.*, in rate of extension, degree of temperature control, which may have affected the respective rates of crystallization[7].

The fact that the saturation values of birefringence are approximately proportional to the changes in density, at all but the lowest extension, is of considerable importance. It shows that the birefringence gives a quantitative measure of the amount of crystallization over a very wide range of elongations. It shows, further, that a very considerable degree of orientation of the crystallites has already been achieved with an extension of only 34 per cent, and that beyond that extension the increase in birefringence is due almost entirely to an increase in the amount of crystalline material, which continues at a fairly uniform rate right to the breaking-point.

The precise meaning to be attached to the phrase "very considerable degree of orientation" requires a detailed examination of the relation between the degree of orientation and the resulting birefringence. Such a theoretical investigation is described in an appendix to this paper. From this it appears that the birefringence is not very sensitive to departures from the state of perfect orientation.

EXPERIMENTS AT 25° AND 50° C

The optical data obtained at higher temperatures will now be considered. Figure 4 shows the variations in birefringence over a period of 1 hour in specimens of crepe stretched to various elongations at 25° C. The following features of these curves should be noted:

1. Below 360 per cent extension, the birefringence tends to fall, the rate of fall becoming less with the lapse of time.

2. From 360 per cent upwards, the birefringence either remains constant or shows a slight increase, this increase being most marked in the early stages.

Corresponding data for a stretching temperature of 50° C are shown in Figure 5. At this temperature, the transition from the falling to the rising type of curves occurs at a higher extension, namely, 680 per cent. Whereas the

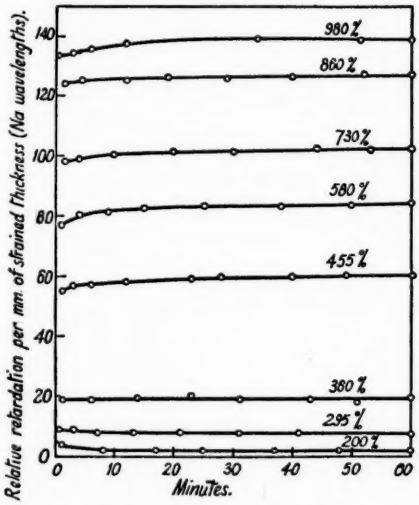

FIG. 4.—Time changes in birefringence in crepe held at the extensions indicated at 25° C.

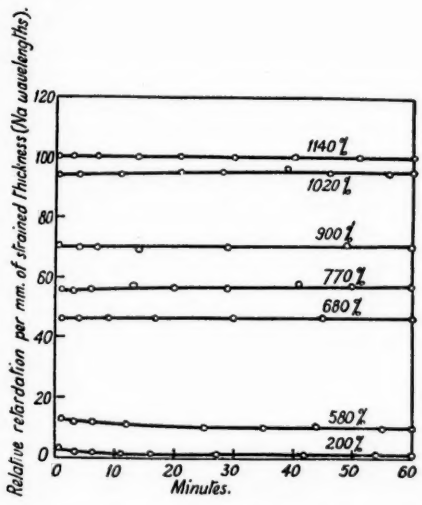

FIG. 5.—Time changes in birefringence in crepe held at the extensions indicated at 50° C.

falling tendency at the lower extensions is more marked at this temperature, the rise at the higher extensions is less conspicuous.

If the birefringence at the end of the 1-hour period is plotted against the elongation (Figure 2, curves *a* and *b*), it is seen that at an elongation corresponding to the transition from the falling to the rising birefringence curve, there is a rapid increase in the magnitude of the birefringence. Following this rather sudden jump, there is a further steady increase as the elongation increases to the breaking-point.

INTERPRETATION OF EXPERIMENTAL RESULTS

The x-ray work of Gehman and Field[8] and others shows that the crystals formed when raw rubber is stretched at room temperature or higher lie with their axes very nearly parallel to the stretching direction, even when the amount of crystalline material is only just sufficient to produce a diffraction pattern. It may, therefore, be concluded that birefringence provides a quantitative measure of crystallization except at low extensions, before the sudden rise. At these low

extensions the optical activity may be due either to incipient crystallization or to a partial alignment of molecules, without crystallization, or to both. The curves show a close resemblance to data on vulcanized rubber given by Thiessen and Wittstadt[6], except that the fall in birefringence corresponding to the lower extensions, which is presumably connected with the release of internal strain, was not present in their case.

From the curves for the higher elongations in Figures 4 and 5, it is seen that the final state of crystallization is not attained instantaneously, although it is approached more quickly at 50° than at 25° C. This may be accounted for by the greater mobility of the molecules at the higher temperature. A similar time-lag in the development of crystallization in vulcanized rubber was observed by Thiessen and Wittstadt[9], using optical methods, and had been demonstrated earlier by Long, Singer and Davey[10] by x-ray methods.

Appearance of Fringes

As at 0° C, the transition from the amorphous to the crystalline state was accompanied by certain characteristic changes in the interference fringes. Whereas at low elongations they were clear and parallel, at intermediate elongations they became less intense and very irregular, indicating that crystallization had not proceeded to the same degree at all points of the rubber. A number of peaks in the fringes could be distinguished, running along the length of the specimen, and suggesting a sort of fibrous crystallization. At higher extensions the fringes became clearer and more regular, although they did not regain entirely their original regularity. The greatest irregularity was observed at extensions of 360 and 455 per cent in the 25° experiments, and at extensions of 580 and 680 per cent in the 50° experiments. These were the regions where the degree of crystallization was changing most rapidly with elongation. These observations indicate that, in the early stages, crystallization is not uniform throughout the rubber, there being comparatively large crystalline patches interspersed with amorphous "spaces". As the extension is increased, these spaces fill up with crystalline rubber, thus producing a more uniform texture.

Check on $B/\Delta\rho$

Since, at these temperatures, the orientation of the crystallites is high, even when the amount of crystallization is small, the change of density accompanying the extension should be proportional to the birefringence, the constant of proportionality having the value found at the higher extensions at 0° C. To check this point, an additional experiment was carried out, in which both the birefringence and the density change were measured on the same specimen of rubber. A strip of crepe film 5 cm. wide and 0.7 mm. thick was extended to 700 per cent elongation, and left for 20 hours at room temperature (about 20° C). A piece was then cut off and examined optically. Since the fringe shift was well beyond the range of the compensator, a number of calibrated cellophane sheets were interposed to bring the dark band into the field of view. The resultant shift, after correction for the spurious displacement of the central band, was 29.4 sodium fringes, the corresponding value of B 106.5 fringes per mm. The uniformity of the crystallization was shown by the fact that, even with this large displacement, the fringes were easily visible, and their displacement was uniform over the whole specimen. The density change, measured on the same specimen at the same temperature, 20° C, was 2.57 per cent, giving $B/\Delta\rho=41.4$. This agrees well with the high-extension values in Table I.

Correlation with Mechanical Properties

The facts brought out in these optical experiments confirm the conclusions arrived at by the author from the study of the plastic flow and recovery phenomena[1]. If, as is believed, the development of crystallization takes place through a grouping together of neighboring portions of long-chain molecules, the effect of crystallization is to increase the cohesion between molecules in certain regions, and thus to increase the effective viscosity of the bulk material. It is, therefore, to be expected that plastic flow will begin to fall at that extension at which crystallization sets in. Using the plastic flow data in the earlier paper, the agreement is found to be reasonably close, as the following table shows.

The birefringence also shows a close correlation with the development of a sharply-defined retraction temperature, a phenomenon directly related to the state of crystallization. It is interesting to note that the existence of such a definite retraction temperature does not imply total crystallization; in fact, the present data, taken in conjunction with the earlier work, show that it may occur when the crystallization has reached no more than 50 per cent of its maximum value.

Table II

Comparison of Optically Determined Crystallization Point with Maximum in Plastic Flow/Elongation Curve

	Temperature	
	25°	50°
Optical crystallization point at elongation of.....	300%	550%
Maximum plastic flow at elongation of.....	300%	450%

With the optical as with the mechanical properties of raw rubber, the rate of extension is of great significance. The above findings hold good only when the elongation is carried out very quickly. This may be illustrated by an experiment in which crepe rubber was extended slowly at 25° C over a period of 30 minutes. In this case crystallization first appeared at an elongation of 600 per cent, compared with 300 per cent in the quick-stretching experiments.

DISCUSSION

x-Ray analysis would appear to offer the best hope of finding a solution to some of the problems raised by the present investigation, particularly the questions of the angular distribution of the crystallites and the proportions of crystalline and amorphous rubber under different conditions of extension. Some interesting work along these lines has already been carried out by Gehman and Field[5], who extended rubber at room temperature and subsequently froze it at −5° C for 18 hours. They were able to demonstrate a gradual transition from the Debye-Scherrer ring pattern, obtained with unstretched rubber, to the fibre pattern as the extension was increased to about 350 per cent. Definite evidence of orientation was observed with an elongation of only 30 per cent. Although obtained under rather different experimental conditions, these data give some support to the conclusions drawn from the present optical experiments.

A view of the underlying process of crystallization which seems to account in a satisfactory manner for many of the observed phenomena has been put forward by Gehman and Field. Starting from Tammann's concept of crystallization in a supercooled liquid, they consider that there are in rubber variations in the local state of order of adjacent molecules or parts of molecules, the most highly

ordered regions acting as incipient nuclei for crystal growth. The probability of the formation of such ordered regions would naturally be increased either by mechanical extension or by a reduction of temperature. Thus at low temperatures "centres, which may consist merely of an approximate parallelism of neighboring portions of long-chain molecules, become effective for crystal growth".

The idea of the growth of crystals around nuclei accounts for the characteristic S-shape of the birefringence and density curves of rubber extended to low elongations at 0° C (Figures 1 and 3). For, if the rate of crystallization is determined by the total surface area of the nuclei at each instant of time, it will obviously increase continuously as crystallization progresses, until the point is reached where the regions of potential growth of the individual crystallites begin to interfere with each other. Beyond this point, the rate of crystallization becomes progressively slower with advancing time.

In contrast to the behavior of an ordinary low-molecular liquid, the crystallization process in a rubber would not be expected to continue to completion. The reason for this difference is to be found not only in the more or less permanent linkages between the long-chain molecules of rubber, which it is necessary to postulate to account for its observed elastic properties, and which will interfere with the proper development of the crystal lattice, but also from the mere fact that the rubber molecule is a long randomly kinked chain. On account of this last fact, it is to be expected that portions of the same molecule may be found in two or more separate crystalline regions. Owing to the restrictions to their movement imposed by their attachment to the crystals, the intervening portions of such molecules will be very difficult to fit into a crystalline lattice. This difficulty will increase rapidly as the amount of crystalline material formed increases, until a point is ultimately reached when further crystallization is no longer possible, even if an important portion of the rubber may still be in the amorphous state.

At low temperatures the application of an extension will not only increase the number of crystal nuclei present, but will also affect their orientation. We have seen that, even at quite low extensions, this orientating effect is considerable. In fact, to account for the optical data, it is necessary to assume that the degree of orientation of the nuclei is very much higher than that of the rubber molecules as a whole. This can be proved indirectly by another observation, namely, that the process of crystallization is accompanied by an increase of length of the stretched specimens. This "secondary elongation", according to Park[11], reaches a maximum of about 4 per cent of the stretched length in the region of 200 to 300 per cent elongation. If the crystal nuclei had the same angular distribution as the molecules as a whole, there would be no reason for a change of shape during crystallization, but if the nuclei are more highly orientated than the molecules as a whole, then, as pointed out by Smith and Saylor[12], an increase of length during crystallization is to be expected.

Another result of extension is to increase the total proportion of material finally brought into the crystalline state. It is suggested that this is due simply to increased alignment of the molecules, which are now more readily fitted into a lattice, owing to the reduction in the number and complexity of the portions of molecules which happen to be in the wrong directions with respect to their neighbors. How closely the state of the rubber at the breaking-point approximates to 100 per cent crystallization cannot be determined from the present experiments, but it is clear that there will always be an appreciable proportion of the molecular chains not fitted into a lattice, however great the extension.

From the picture of the semicrystalline state of rubber thus arrived at, it is

not difficult to understand why comparatively little crystallization exerts such a profound effect on plastic flow. It is seen that, on account of the molecular ties between the crystals and the amorphous rubber, or directly between crystals, freedom of movement of crystals one over another is greatly impeded. Mechanically, the crystallization may be regarded as introducing a large number of new cohesional linkages between molecules. It is the number and strength of these cohesional linkages which determines the bulk viscosity of the material. If this picture is correct, it follows that the transition from a given partially extended crystalline state to a state of higher (or lower) extension cannot be brought about simply by rotation of the crystals already formed. Some degree of breakdown of the original crystal pattern will necessarily be required in order that the molecules may move into the new positions which the extension forces them to take up. This effect may be observed through its influence on the birefringence. In a particular experiment, a piece of rubber which had been extended to 260 per cent elongation and allowed sufficient time at 0° C for completion of crystallization was subjected to a further deformation at this temperature, whereby its elongation was increased to 470 per cent (compared with the unstretched length). In spite of the increased elongation, the birefringence immediately fell, and it was only after the lapse of time that it eventually rose to a value higher than that which it possessed at the original elongation.

Minimum Density of the Rubber Crystal

It has already been stated that the present experiments do not provide any means of determining the absolute, as distinct from the relative, amounts of crystallization in rubber. It is, therefore, not possible to determine the density of the rubber crystal, because, even under the most favorable conditions, there remains an unknown proportion of uncrystallized material. It is possible only to assign a lower limit to this density.

The highest state of crystallization was achieved at 870 per cent extension at 0° C, an extension very near the breaking-point. The birefringence in this state was 155.0 sodium wave lengths per mm. Taking 41.4 as the best value of $B/\Delta\rho$ in this region, the corresponding value of $\Delta\rho$ is 3.75 per cent. The amorphous rubber used in these experiments had a density of 0.924_5 at 0° C. The minimum density of the rubber crystal at 0° C is thus 0.959_2. This figure might be further increased if allowance could be made for the presence of a proportion of nonrubber components in the crepe. The density of pure rubber appears to be no different from that of the crude material (Wood)[6], but the impurities must reduce to some extent the maximum degree of crystallization achieved. Bekkedahl[5], for instance, has shown that, for crystallization in the unstretched state, the change of density is greater with purified rubber than with smoked sheet.

Even without this correction the change of density of 3.75 per cent, calculated from these experiments, is higher than any directly measured change previously published. It is interesting to note, however, that Van Rossem and Lotichius[13] observed an increase of density of 3.1 per cent in rubber which had been "frozen" for several years, a figure noticeably higher than that previously given by Bekkedahl.

APPENDIX. EFFECT OF ORIENTATION ON BIREFRINGENCE

To examine the effect of the orientation factor on birefringence, a calculation was made of the fringe shift to be expected when polarized light is passed through

a number of superposed birefringent crystals variously orientated. For this purpose it was necessary to make an arbitrary choice of the law according to which the crystal axes are distributed in angle; the manner of making this choice obviously will not affect the general nature of the result obtained. The type of distribution chosen is illustrated in Figure 6. It was obtained simply by projecting a circle containing the appropriate number of equally spaced diameters into an ellipse. The degree of orientation is characterized by the parameter a/b, the ratio of the principal axes of the ellipse.

The calculation was made for a succession of 10 crystals, each introducing a phase difference p between the two components of light transmitted through it. The light was then assumed to pass through a quartz wedge, introducing a phase difference q, and finally through the analyzing Nicol. The analysis yielded a number of terms representing components of the transmitted light having phase shifts O, p, $2p$, . . . $10p$, and q, $p+q$, . . . $10p+q$. A graphical combination

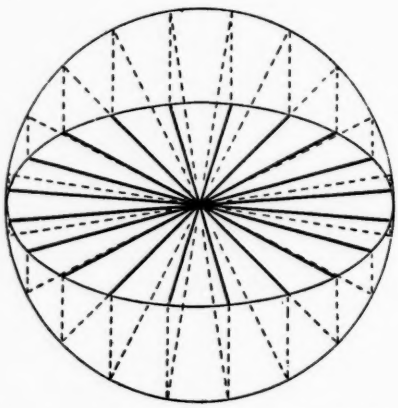

FIG. 6.—Illustrating type of angular distribution assumed.

of these terms then yielded, for any value of p, the corresponding value of q required to make the resultant intensity a minimum, *i.e.*, the compensator setting for a dark band. This will be referred to as the resultant phase shift.

Taking first a uniform distribution of the crystal axes, corresponding to zero extension, the resultant phase shift was calculated for $p=30°$, using three different random orders of succession. The values obtained were, respectively: 0°, +4° and −5°, the average numerical value being, therefore, 3°. This is only 1 per cent of the total phase shift which would occur if all the crystal axes were in the same direction, and confirms that the model chosen contains a sufficiently large number of crystals to yield results of statistical accuracy. With a larger phase shift per crystal, namely 60°, the effect of the particular order of succession chosen was apparent, and with $p=120°$ the model became unworkable. The results are, therefore, applicable only for small values of p, which means in practice that the crystals must be small.

Taking a particular random order of succession, the resultant phase shift was then calculated for different values of a/b, the phase shift per crystal being 30°. The results of these calculations are given in Figure 7. The curve starts from the origin, and approaches the limiting value of 300° for large values of a/b.

This shows that the birefringence is insensitive to small departures from perfect orientation.

It is not possible to relate a/b directly to elongation, but it may be assumed that a plot of the resultant phase shift against elongation, instead of against a/b, would yield a curve of the same general form. To obtain the form of the birefringence-elongation curve when both the orientation and the proportion of crystalline material depend on elongation, some assumption must be made as to the dependence of the second of these two factors on elongation. If we assume that the total percentage of crystalline material is a linear function of

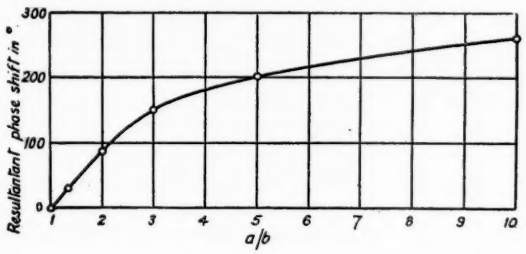

FIG. 7.—Birefringence calculated on 10-crystal model. Phase shift per crystal = 30°.

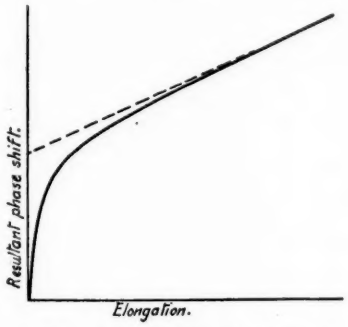

FIG. 8.—Expected birefringence-elongation curve from combined effect of orientation and increase of quantity of crystalline material.

elongation, the birefringence-elongation curve will take the form shown in Figure 8. This agrees well with the experimental curve over its linear portion, but not over its curved portion (*cf.* Figure 2*c*). To account for the whole of the experimental data, it is necessary to assume that the curved portion occurs wholly below the lowest extension at which observations were made, that is to say, a considerable orientation has already taken place at this low extension. The analysis, therefore, leads to the same conclusions as those arrived at from consideration of the density changes.

SUMMARY

The process of crystallization in raw rubber held at various extensions at 0° C has been studied by following the accompanying changes in double refraction and in density. From a comparison of the two sets of data, it is concluded that a

very low extension produces a relatively high degree of orientation of the axes of the crystallites in the direction of the extension. From 100 per cent extension to the breaking-point, the increase in birefringence with elongation is due almost entirely to an increase in the proportion of crystalline rubber present; over this range the birefringence therefore gives a quantitative measure of the amount of crystallization.

From the study of birefringence at 25° and 50° C, it appears that crystallization sets in rather rapidly at a certain intermediate elongation, and then increases continuously to the breaking-point. The observed changes in crystallization show a close correlation with plastic flow and elastic recovery phenomena.

The bearing of these observations on the molecular structure of rubber and its mode of crystallization is discussed. It is estimated that the increase of density of rubber on crystallizing is not less than 3.75 per cent.

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COMPARISON BETWEEN THE OBSERVED DENSITY OF CRYSTALLINE RUBBER AND THE DENSITY CALCULATED FROM X-RAY DATA *

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INTRODUCTION

When unvulcanized rubber is stretched quickly, an orientation of structure occurs parallel to the direction of extension. This orientation is usually regarded as a form of crystallization, because of the optical and other phenomena which accompany it. It is also accompanied by a change of volume. When unstretched rubber is subjected to suitable temperatures below about 10° C, it too becomes crystalline. The crystallization of rubber is accompanied by an increase of density, and the simultaneous production of an x-ray diffraction pattern is usually interpreted as evidence that crystallization has occurred. A diffraction pattern of this kind results from regular repetition, within the crystal structure, of groups of atoms or molecules in a definite spatial arrangement. The smallest group from which the structure can be built up in this way is called the unit cell; and the dimensions can be computed from measurements of the pattern, provided it is possible to determine the crystal form. The pattern of stretched rubber consists of interference spots, and that of frozen rubber consists of rings, but both of their measurements have been shown to indicate the same unit cell. If, in addition, the number of atoms in the unit cell is known, the density of the material can be computed. If the computed density agrees with that found by direct measurement, the fact is a valuable indication of the correctness of the assumed structure on which the calculation of density was based. Accurate knowledge of the density of completely crystallized rubber would therefore serve both as a guide in studies of structure and as a measure of the degree of crystallization of any material under consideration.

In the experimental work described in this paper, the rubber was crystallized as completely as possible. Its density was determined by recognized methods, and compared with the densities calculated from x-ray measurements.

REVIEW OF PREVIOUS WORK

The densities obtained by calculation from x-ray investigations have recently been summarized by Gehman[1]. The values vary with the assumptions regarding the unit cell. Until lately they were greater than unity but have tended to decrease in the course of more recent work. The lowest value found in the literature now is 0.965[2]. The densities measured directly have been less than the computed values, and the differences have been difficult to explain. Perhaps further interpretations of x-ray patterns will reconcile them.

The rhombic cell postulated by Mark and von Susich[3], which undoubtedly had an influence on the configurations assumed in later hypotheses, required that

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crystallized rubber should have a density of 1.08. According to later measurements of Lotmar and Meyer[4], who assumed that the cell is monoclinic, it should be 1.02. Sauter[5] described another rhombic cell based on the assumed existence of a double reflection. The density computed from this cell is 0.974. Morss[2] attempted to find the true unit cell of rubber, but his conclusions were not entirely satisfactory. The basis of his deductions is a change from 90° to 109.5° of the angle between the two independent sets of planes which reflect the two strong equatorial spots. With this modification, the calculated density of the unit cell is 1.00. When Morss applied the angle 109.5° to the measurements of Lotmar and Meyer, the value was 0.965. Misch and van der Wyk[6] have recently obtained photographic evidence of the double reflection which was assumed to exist by Sauter. The cell they postulated resembles that of Morss, but contains 16 isoprene units; the calculated density is 0.970.

In the publications of Lotmar and Meyer and of other investigators mentioned above, it is evident that the density 0.965 was accepted as the value to which the unit cell of rubber should conform. This same value was observed by direct measurement by Kirchhof[7], who used smoked sheet which had been stretched to 900 per cent elongation and had then been subjected to a fitting low temperature for further possible crystallization. In the unstretched amorphous state, the density of his material was 0.942. As this value is considerably higher than any of those listed by Wood[8], and as no temperature is mentioned, the determination was probably made at temperatures lower than 25° C, or the smoked sheet may have contained abnormally heavy impurities. Lotmar and Meyer, however, obtained the same experimental value as Kirchhof with a crystalline material which was prepared by evaporation of a solution of rubber in benezene, and subsequently crystallized, but they also did not mention the temperature of measurement. The rubber was held in a well-stretched state at 0° C for 24 hours before the determination.

EXPERIMENTAL WORK

1. Preparation of Material

Because impurities are disregarded in calculating the density of rubber from x-ray measurements, it was believed desirable to purify rubber for direct determinations. Feuchter[9] has shown that sol fractions of raw rubber are almost free from nitrogen and otherwise quite pure. Accordingly, in the work to be described, unstretched and stretched petroleum ether-sol fractions were used. Smoked sheet and dried latex were also examined for comparison. The rubber used to prepare the petroleum ether-sol had received the following treatment. The latex of *Hevea Brasiliensis*, protected from contamination by bacteria with sodium ethylmercurithiosalicylate, was digested with trypsin to degrade the protein in the latex. The water-soluble products of this treatment were largely removed by creaming the rubber three times with a 0.2 per cent solution of sodium alginate, and withdrawing the layer beneath the creamed material. A small amount of natural antioxidants, equivalent at least to that in raw rubber[10], was added to the rubber dispersion after each separation. After the third separation, the upper layer was centrifuged to remove dirt, and was then diluted with distilled water until it contained about 1 per cent of rubber. By freezing the diluted dispersion, a loose porous coagulum was formed; after the ice had melted, residual water-soluble impurities were removed by washing the coagulum with successive portions of distilled water. From the dried product a petroleum ether solution of sol was prepared by a procedure similar to that used earlier.

After the sol fraction was separated from the gel, the petroleum ether was removed by evaporation. Films formed by the evaporation of solutions of rubber in benezene at room temperature were usually free from air bubbles. The residue of sol rubber was dissolved in benzene of reagent quality, and the solution was transferred to an evaporating dish. Transparent, colorless films were formed about 2 mm. thick. Rubber which had deposited on the sides of the dish was cut away. The dish was placed in distilled water, and when the deposit on the bottom could readily be detached, samples weighing between 1 and 1.5 grams were cut to a suitable shape under water. The samples were dried to constant weight at 100° C in a stream of nitrogen.

With the purpose of increasing mobility during crystallization at a suitable low temperature, a plastic rubber was prepared by disaggregating, with piperidine, a sol fraction dissolved in benzene. The piperidine was subsequently extracted from the product with successive portions of acetone at room temperature. After the disaggregated rubber had been chilled at −10° C for 30 minutes, it could be elongated to at least twice its original length.

2. Methods of Crystallization

The marked discrepancy between the calculated and experimentally determined values persisted in spite of the precise x-ray measurements of Lotmar and Meyer, and may well cast doubt on the experimental value if the assumptions leading to the calculation of the axes of the unit cell are accepted. Consequently it seemed possible that, by some special experimental procedures, rubber could be crystallized to a higher degree and thus have a higher determined density than any reported in the literature. Some of the procedures were based in part on the concept of the rubber molecule as a long chain with angular configuration. The chains, if they are assumed to exist as a tangled, interlacing mass and to possess secondary valence forces, can perhaps be oriented with difficulty. It was thought that very slow elongation might cause more perfect alinement because, under this condition, the forces of attraction and repulsion along the sides of the molecule would be given greater freedom. Strips about 25 mm. wide and 1 mm. thick were stretched at various slow rates, at room temperature and also at −10° C and at −20° C, immediately after they had become chilled. To determine the effect of rapid stretching, other strips were extended suddenly at these temperatures. According to another concept of rubber structure, needle-shaped molecules may exist in groups of micelles. During disaggregation, separation of the molecules might be expected to occur, accompanied by increased mobility. Strips of disaggregated rubber were chilled to −10° C and to −20° C to decrease mobility and minimize any disorganization caused by the heat of stretching, and then stretched quickly to their maximum elongations. Others were stretched in successive small steps to their maximum elongations during 20 minutes before crystallization became pronounced. None of the various special methods described above had any effect. The samples with which the results in Table I were obtained had been subjected to temperatures of about −15° C for different periods, none longer than 30 days, before the determinations were made.

3. Methods of Determining Density

The densities were determined by the hydrostatic method in an immersion mixture consisting of equal parts by weight of acetone and water. They were also determined by adjusting the proportions of acetone and water until the mixture had the same density as the specimen, and the density of the mixture

was determined. The hydrostatic method involved the use of an analytical balance. A strip of rubber about 70 mm. long, which had been cut with chilled shears, was held on a stiff platinum wire, the end of which was bent to form a rigid support. The immersion mixture was contained in a Dewar flask, and its density was found with a precision type of Westphal balance, suitably corrected. The determinations were made usually to about one-thousandth of a unit. If greater precision was desired, the effect of the cold immersion mixture on the arm of the balance was noted, a small amount of a suitable wetting agent was added to minimize surface drag on the wire, and the observations were made as rapidly as possible. Since some forms of crystalline rubber have at times been observed to melt below 0° C, a temperature of −10° C was used in this work for density determinations of crystalline material to avoid melting and also to suppress the tendency of the rubber to swell in the acetone-water mixture. With

TABLE I

DENSITIES OF AMORPHOUS RUBBER AND OF CRYSTALLINE RUBBER AT −10° C

[The densities of amorphous rubber at −10° C were calculated from values obtained at 25° C]

Petroleum-ether sol		Smoked sheet			
				Crystalline stretched (−10° C)	
Amorphous unstretched (−10° C)	Crystalline unstretched (−10° C)	Amorphous unstretched (−10° C)	Crystalline unstretched (−10° C)	Density	Elongation (per cent)
0.928	0.946	0.932	0.951	0.954	100
—	0.945	—	0.952	0.956	200
—	0.944	—	0.951	0.956	300
—	0.943	—	0.950	0.956	400
—	—	—	—	0.956	500
—	—	—	—	0.957	600
—	—	—	—	0.957	700
—	—	—	—	0.957	800
—	—	—	—	0.958	900
—	—	—	—	0.958	1,000
—	—	—	—	0.960	>1,000

amorphous rubber, a temperature of 25° C was used, and the sample was attached to a sinker in distilled water as the immersion liquid. Air which abhered to the surface of a specimen immersed in water, or in a mixture of water and acetone, was removed. After a determination of density, the sample was dried in air and placed in dimethyl phthalate, which has approximately the refractive index of rubber. Air in the sample was readily observed and, when necessary, the amount of it was estimated[17]. The highest correction applied to the density because of included air was 0.001.

RESULTS FROM DENSITY DETERMINATIONS

Typical values of the density of amorphous rubber and of crystalline rubber at −10° are given in Table I. With crystalline unstretched smoked sheet, the results vary between 0.950 and 0.952; with crystalline unstretched petroleum-ethersol, they range from 0.948 to 0.951. The results which show the effect of stretching on smoked sheet represent successive elongations of 100 per cent. The increase in density is slight, *i.e.*, not more than 0.01. The last value, 0.960, was obtained with a sample extended beyond 1,000 per cent, almost to the breaking point. Densities higher than 0.960 were possible only by racking the

rubber. The density of amorphous smoked sheet at −10° C is calculated by the formula of Bekkedahl[11], using the value 0.906, which was observed at 25° C; that of amorphous sol rubber from 0.902, the highest density observed with this material at 25° C. This value is lower than any of the values listed by Wood[8]. However, in addition to this value of 0.902, other densities were observed ranging as low as 0.899 with different lots of sol rubber. Repeated observations with any single perparation agreed to the third decimal place. In spite of attempts to find a source of error, the differences in different lots of sol rubber persisted.

In addition to the values listed, some determinations were made with miscellaneous samples prepared in various ways. When dried strips, prepared by the evaporation of dialyzed latex, were extended to various degrees between 100-per cent and 1,000-per cent elongations, and were subjected to a temperature of −15° C while stretched, their densities were the same as those observed when smoked sheet was elongated (Table I), and stretching caused an increase of not more than 0.01. The density at −10° C of disaggregated rubber after chilling was 0.951, which is in the range observed with sol rubber. That of smoked sheet which had been stored without pressure at 0° C for approximately 5 years was 0.957 at −10° C. To determine the effect of pressure in the absence of orientation, sol rubber was placed in a square, confined space with sides about 1 sq. cm., and squeezed by a piston under a pressure of about 1,000 atmospheres, at room temperature for 8 hours. While the pressure was maintained, the rubber was crystallized during 12 hours, at −10° C. Its density was 0.951. The same value obtained without pressure is listed in the table of results. Pressure from all sides of the confining space did not in this case increase the density.

The rate at which rubber crystallizes at −20° C was observed with unstretched specimens cut from adjacent areas of a smoked sheet. The initial density, 0.929, of amorphous rubber at −20° C was calculated from Wood's publication[8] on physical constants of rubber, because crystallization occurred during attempts to determine it. The densities at successive intervals were as follows: after 3 hours, 0.935; 5 hours, 0.950; 24 hours, 0.955; 1 week, 0.955. When these values were plotted, a curve was obtained which was similar in shape to that reported by Bekkedahl[11] for the rate observed at 0° C. At −20° C the transition was faster.

In earlier work[12] stretched rubber, maintained in an extended state, was observed to increase in length when subjected to suitable low temperatures. According to the explanation which was suggested, stretching establishes a crystal lattice with crystals oriented parallel to the direction of elongation, and when more molecules enter it, they too assume the parallel direction. The rubber elongates because of the shape of the molecule until molecular movement is inhibited by random crystallization of the residual rubber. To determine whether a marked change of density occurs during the secondary extension, the following procedure was used. A strip of uniform width and thickness from dried latex was extended, fastened at both ends and at the middle, forming two sections, and immediately exposed to a temperature of −20° C. When the extension had definitely commenced, a specimen was cut from one section, and its density was determined as quickly as possible by the hydrostatic method, to a ten-thousandth of a unit. After the extension had become completely established, about 20 minutes later, a specimen from the second section was examined. The elongation was the difference between the length of the specimen after its density had been determined, and the length after the specimen had subsequently been allowed to retract at room temperature for 24 hours. With one sample the density before secondary extension was 0.9449 and the elongation 380 per cent; at maxi-

mum secondary extension it was 0.9456 at an elongation of 440 per cent. With another sample the density before secondary extension was 0.9386 at 130 per cent elongation, and 0.9391 afterward at 195 per cent elongation. The increase of density with the first sample, 0.0007, during a secondary extension of 60 per cent, amounts to 0.0071, when the increase is based on 1,000 per cent elongation minus the original elongation before secondary extension took place. The increase of density of the second sample, 0.0005, during a secondary extension of 65 per cent, becomes 0.0067 on the same basis. These increases agree closely with the results obtained with smoked sheet, based on 1,000 per cent elongation, in Table I. There the minimum increase is 0.006 and the maximum 0.008.

DISCUSSION OF RESULTS

The change of volume which takes place during the elongation of rubber appears to be the result of the formation of crystals of the same type as those formed when rubber is cooled. The fact that calculations of the dimensions of unit cells from x-ray data lead to the same result in the two cases suggests this. The increase of density during elongation is usually ascribed to a form of packing in crystallization of an oriented fibrous type, which takes place. The increase continues during racking, but becomes constant at 2,000 per cent elongation, at which Feuchter[13] found a density of 0.953, apparently at some room temperature. If a probable temperature of 20° C is assumed, at −10° C it would be 0.970.

If density is to be used to aid in the interpretation of x-ray diffraction patterns, the effect of temperature should not be disregarded, because rubber has a large coefficient of expansion.

The density of rubber, completely crystallized when stretched, appears to be the limiting density reported by Feuchter, for the following reason. In x-ray diagrams of stretched rubber, the position of the diffraction spots is independent of the elongation, but the spots become more intense as the elongation increases, *i.e.*, with increase of packing. This suggests that the maximum effect represents an orientation that is substantially complete. Recently, Field[14] developed a method of measuring the amount of crystallinity in stretched rubber. At high elongations the maximum found was about 80 per cent of the total. For total crystallinity a density of 0.965 was deduced. Treloar[15] estimates that the increase of density during crystallization is not less than 3.75 per cent. The reports of several observers who have examined types of sol and gel rubber of varying degrees of aggregation by x-ray technique indicate that crystallinity is developed and retained most readily in the stretched gel fraction. Consequently, when rubber is stretched, there appears to be a relation between the degree of polymerization and the amount of crystalline material formed.

The range of densities, 0.899 to 0.902, observed with amorphous petroleum-ether sol rubber in this work is much less than the differences shown by results reported in the literature and summarized by Wood[8]. The following values are quoted from the summary. With unpurified rubber at 25° C, Bunschoten found a density of 0.905; Whitby, 0.906; McCallum and Whitby, 0.918; and Feuchter, 0.928. With purified rubber at the same temperature, Weber found 0.905; McPherson, 0.906; McCallum and Whitby, 0.9207; and Bondy (Staudinger), 0.9208. Recently Kemp[16] reported densities of petroleum-ethersol rubber, determined at 20° C, which varied from 0.905 to 0.910. At 25° C, this corresponds to a density range from 0.902 to 0.905. With impure and with purified material, the lack of agreement is significant, and the densities of sol rubber, 0.899 to 0.902, agree with none of the values quoted. Perhaps the low values obtained in this work repre-

sent the densities of depolymerzide material. By this term is meant a disruption of long-chain molecules into short ones, characterized by lowered viscosity, molecular weight and decreased tensile strength. In long-chain molecules of high molecular weight, for example, 100,000, forces of attraction and repulsion at the ends must be negligible. The molecule substantially is one consisting of two sides. If the long molecule is broken into many short ones, it is possible that disruption may continue until the ends of short molecules cause significant attraction and repulsion. An increase of volume would result. Unfortunately, nothing is known about the degree of depolymerization which is necessary to cause a change of volume. Furthermore, any proposed explanation for the ranges of density observed must be viewed with skepticism, because no structure which has been proposed for rubber has received complete acceptance.

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EFFECT OF REINFORCING PIGMENTS ON RUBBER HYDROCARBON *

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Several investigators[20] have established that sulfur vulcanization of rubber involves chemical combination of sulfur and rubber hydrocarbon. A definite decrease in unsaturation of the rubber hydrocarbon as vulcanization progresses has been generally noted[3, 10, 18].

While it has often been concluded that a double bond is saturated for each atomic equivalent of combined sulfur[10, 18], recent work by Brown and Hauser[3, 7] demonstrates that this conclusion cannot be applied in all cases. In certain compounds they found the loss in unsaturation with extent of vulcanization to be considerably less than anticipated on the basis above. Their results indicate that stocks reaching optimum cure with the least loss of unsaturation possess the greatest tensile strength.

Although a considerable amount of work has been done on this problem, we have not found a published account of similar investigations performed on stocks containing significant loadings of reinforcing fillers. Since, as pointed out below, the nature of the bonding between such fillers and the rubber molecules has not been clearly defined, one is not justified in applying previous results obtained on stocks containing no reinforcing fillers to those bearing appreciable loadings of such substances. Accordingly one portion of the present investigation was concerned with determining the effect of various fillers on the course of sulfur vulcanization, as judged from combined sulfur and unsaturation values.

As pointed out by Gehman and Field[6] it is undoubtedly true that the black particle in a carbon-black-reinforced rubber stock is firmly attached to the rubber molecule. The nature of the bonding between the black and rubber has not been clearly defined. Some investigators[4, 8, 14, 17] maintain that the association is physical and involves definite forces of adhesion or adsorption; others[13] have suggested the formation of primary valence linkages with rubber hydrocarbon. The opinion of the present authors is that if such linkages are formed, the ethylenic bonds of the rubber molecule would probably be involved. If this latter view is correct, then a specific loss in unsaturation of rubber hydrocarbon, due to the reinforcing filler, should occur. Thus the second objective of the present study was to determine whether it was possible by chemical means to detect such a linkage. If measurable, this effect, together with the surface area determinations reported previously[15], would be particularly valuable in estimating the reinforcing value of various fillers.

EXPERIMENTAL PROCEDURE

The unsaturation of the rubber stocks was determined by addition of iodine chloride. The procedure followed was essentially Kemp's technique[9, 11] as modified by Blake and Bruce[2].

A 0.1-gram sample of stock was dissolved in boiling *p*-dichlorobenzene. This

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usually required from 2 to 3 hours. Solution became more difficult with well cured compounds. This was overcome by freezing the sample with solid carbon dioxide, and sectioning on a microtome. These finely shaved sections dissolved readily, and no further difficulty was encountered. When the sample had dissolved, it was allowed to cool, and was then taken up in carbon disulfide and further cooled to 0° C. Twenty-five cubic centimeters of 0.2 *N* iodine chloride were then added, and the reaction was allowed to progress for 2 hours at 0° C. Ten cubic centimeters of 1.2 *N* potassium iodine and 25 cc. of ethanol were added, and the iodine liberated from the excess iodine chloride was titrated with 0.1 *N* sodium thiosulfate. A blank was run and, from the difference, the amount of iodine chloride combined was calculated.

Kemp[10] showed that carbon black, glue, cellulose, and inorganic compounding ingredients have no effect on the determination. In agreement with Kemp, we found that, although a reinforcing channel black removes about 11 per cent iodine chloride from a 0.2 *N* solution, it is only physically adsorbed, as evidenced by the fact that the entire 11 per cent could be titrated back with sodium thiosulfate.

TABLE I

UNSATURATION OF NATURAL AND SYNTHETIC RUBBERS

	Grams of iodine per 100 grams rubber	Percentage unsaturation
C_5H_8 (theoretical)	372.8	100
Pale crepe	359	96.3
Pale crepe (milled)	359	96.3
Pale crepe (cold-extracted)	367	98.3
Smoked sheet	357	95.7
Hycar-OR	191	—
Vistanex	2.5	—

The other pigments employed were similarly shown to be chemically inert toward iodine chloride.

The fillers employed in the present investigation included a standard rubber-reinforcing channel black with a surface area of 110 M^2 per gram, a German reinforcing black (CK-3) with a surface of 98 M^2 per gram, and kaolin with a surface of 20 M^2 per gram. A single supply of washed pale crepe was used throughout the investigation. Combined sulfur was determined by first extracting the free sulfur with acetone and then oxidizing the extracted stock with concentrated nitric acid and potassium chlorate, according to A. S. T. M. procedure D 297[1]. The combined surfur was precipitated and weighed as barium sulfate. The rubber stocks were mixed on a 12-inch laboratory open mill at 140° F. After 3 hours of cooling they were remilled and with the exception of the 10 per cent sulfur stocks, cured at 274° F on a laboratory steam press. The 10 per cent sulfur stocks were cured at 300° F.

The iodine values reported in Table I are based on 100 grams of rubber. The per cent unsaturation was calculated by comparison with the value 372.8 grams of iodine added per 100 grams of pure rubber hydrocarbon[2, 11]. The iodine values reported in Table III for the compounded stocks are as determined per 100 grams of compound. From the known composition of the stocks, the iodine value per 100 grams of rubber was computed and the per cent unsaturation calculated by comparison with the value 372.8.

RESULTS

Table I contains unsaturation values for the pale crepe employed in the present investigation, which are in agreement with previously reported values[2, 9, 11]. The nearly complete saturation of Vistanex is in agreement with its recognized resistance to deterioration, as well as its inability to vulcanize with sulfur[12, 16]. Similarly the lower unsaturation value for Hycar-OR is in agreement with its compounding properties[5].

Table II describes the rubber compounds employed in the present investigation. All recipes are described on a weight basis. The data collected are presented in Tables III and IV. Compound A, consisting simply of 100 parts by weight of pale crepe and 45 parts by weight of black, shows no significant alteration in unsaturation on heating at 274° F for the times indicated. Compound C, consisting of 3 parts of sulfur and 100 of pale crepe, shows a definite loss in unsaturation with time of cure. As Figure 1 shows[21], this loss in unsaturation is accompanied by an increase in the amount of combined sulfur. However, the loss in unsaturation is considerably greater than can be accounted for by assuming that one sulfur atom saturates a single double bond. In this low-sulfur

TABLE II

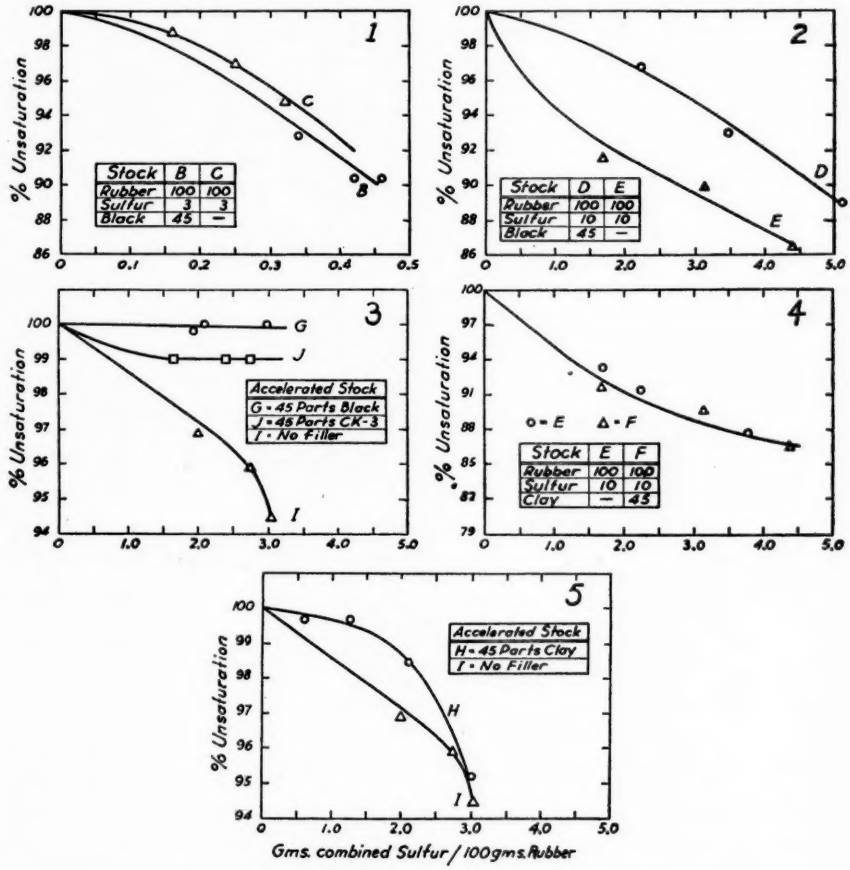
COMPOUNDS INVESTIGATED

	A	B	C	D	E	F	G	H	I	J
Pale crepe	100	100	100	100	100	100	100	100	100	100
Zinc oxide	—	—	—	—	—	—	5	5	5	5
Sulfur	—	3	3	10	10	10	3	3	3	3
Pine tar	—	—	—	—	—	—	3	3	3	3
Mercaptobenzothiazole	—	—	—	—	—	—	0.9	0.9	0.9	0.9
Stearic acid	—	—	—	—	—	—	4	4	4	4
Agerite-Hipar	—	—	—	—	—	—	1	1	1	1
Filler										
Channel black	45	45	—	45	—	—	45	—	—	—
Kaolin	—	—	—	—	—	45	—	45	—	—
CK-3 black	—	—	—	—	—	—	—	—	—	45

compound, only about 12 per cent of the available sulfur has combined at the longest cure. To study the relationship at concentrations of combined sulfur approaching those encountered in commercial tread stocks, compound E was prepared containing 10 parts of sulfur to 100 of rubber. The results for cures up to 120 minutes are presented graphically in Figure 2. In this case nearly 50 per cent of the total sulfur has combined in 120 minutes at 300° F. The data indicate one sulfur atom saturating between one and two double bonds. The next compound studied, I, was a typical accelerated tread stock recipe, with the usual 45 parts of reinforcing agent omitted. It was cured for 30, 60, and 90 minutes. After a 60-minute cure, over 90 per cent of the sulfur has combined, and the unsaturation drops rapidly (Figure 3). Hauser and Brown[7] noted this loss in unsaturation after most of the sulfur in the stock had combined. They suggest that it may be due to polymerization of the rubber. Our data on compound A indicate that, on prolonged heating, some loss of unsaturation of rubber may occur in the absence of sulfur. The effect, however, is small, and may not be real. In any case it is too slight to account for the anomalous drop in unsaturation on overcure shown by sulfur-bearing compound I. This, however, does not mean that the possibility of extended polymerization on overcure in sulfur-bearing stocks is excluded, since the presence of a definite amount of combined sulfur may be essential for the initiation of such a reaction.

The data for compound I indicate a loss of somewhat less than one double bond for every atom of combined sulfur before the sudden drop of unsaturation on overcure.

To certain of the above compounds various fillers were added, as shown in Table II. Unsaturation and percentages of combined sulfur were again determined for various times of cure, as recorded in Tables III and IV. From Figure 1 it


1
% Unsaturation
Stock | B | C
Rubber | 100 | 100
Sulfur | 3 | 3
Black | 45 | —
2
Stock | D | E
Rubber | 100 | 100
Sulfur | 10 | 10
Black | 45 | —
3
Accelerated Stock
G - 45 Parts Black
J - 45 Parts CK-3
I - No Filler
4
○ - E △ - F
Stock | E | F
Rubber | 100 | 100
Sulfur | 10 | 10
Clay | — | 45
5
Accelerated Stock
H - 45 Parts Clay
I - No Filler
Gms. combined Sulfur / 100 gms. Rubber

FIGS. 1 to 5.—Unsaturation values for the various compounds.

is evident that the addition of 45 parts of channel black to compound C has not greatly altered the unsaturation-combined sulfur ratio. [The accelerating effect of carbon black on cure, as pointed out by Wiegand[19], is evident in compounds B and C. Compound G, on the other hand, shows the familiar retarding effect experienced with stocks containing added organic accelerators.]

The amounts of combined sulfur found in compound B were only one-tenth of those normally found for similar cures in accelerated tread stock compounds. Accordingly compound D was prepared with 10 parts of sulfur to obtain comparisons with accelerated compounds at about equal concentrations of com-

bined sulfur. As Figure 2 shows, a definite effect of carbon black is now apparent. For a given amount of combined sulfur, the black-bearing stock D shows considerably less loss in unsaturation than the pure gum stock E.

The next stock studied was a typical accelerated tread stock, G, containing 45 parts of channel black. The results are plotted in Figure 3, together with stock I, from which the black was omitted. The effect of reinforcing carbon black in this compound is most striking. As Figure 3 shows, no significant loss in unsaturation of the carbon-black-bearing stock could be detected over any of the cures studied. This is in striking contrast to compound I, which contains no reinforcing agent, and which shows a marked drop in unsaturation over the same range of cures. This range, as is evident from Table V, includes all cures of technical significance. In compound J, 45 parts of German naphthalene black CK-3 were substituted for channel black. As Table V shows, CK-3 has com-

TABLE III

UNSATURATION VALUES

Time of cure (min.)	A		B		C		D		E	
	I_2 value	% unsatn.	I_2 value	% unsatn.	I_2 value	% unsatn.	I_2 value	% unsatn.	I_2 value	% unsatn.
0.....	258	100	257	101.8	360	99.5	237	99.0	335	99
20.....	—	—	—	—	—	—	—	—	—	—
30.....	260	101	—	—	—	—	—	—	—	—
40.....	—	—	—	—	—	—	—	—	—	—
60.....	260	101	239	94.8	357	98.8	231	95.8	307	90.6
75.....	—	—	—	—	—	—	—	—	—	—
90.....	253	98.5	237	92.8	352	97.0	221	92.0	301	88.7
120.....	—	—	234	92.5	343	94.8	212	88.2	290	85.5
	F		G		H		I		J	
0.....	238.5	99.2	229	99.2	230	99.5	315	98.9	232	100.3
20.....	—	—	—	—	229	99.2	—	—	—	—
30.....	—	—	228	99.0	—	—	306	95.8	229	99
40.....	—	—	—	—	229	99.2	—	—	—	—
60.....	222	92.5	230	99.5	—	—	302	94.8	228	99
75.....	—	—	—	—	226	98	—	—	—	—
90.....	218	90.7	229	99.2	—	—	297	93.4	228	99
120.....	209	86.8	—	—	218.5	95.0	—	—	—	—

pounding properties approaching those of American channel black. The slight drop in unsaturation indicated in Figure 3 for the 30-minute cure is probably experimental error, since no further decrease could be detected with increasing amounts of combined sulfur. The method of manufacture and raw material used in the preparation of these two reinforcing carbon blacks are quite different, yet their effect in preventing loss of unsaturation of the rubber stock on vulcanization is the same. Accordingly, this effect is not peculiar to channel blacks prepared from natural gas, but appears to be general for reinforcing pigments.

Various grades of channel blacks with differing processing and curing characteristics are available to the rubber industry. The present investigation was extended to include some of them. Detailed results are not included here, since over the range of commercial rubber blacks studied no essential differences were noted from those obtained with the grade-6 black reported in Table III.

All the pigments so far studied exert a definite reinforcing effect in rubber and in each case, during vulcanization, no real loss in unsaturation was observed with increasing amounts of combined sulfur. To observe whether this

effect is characteristic only of reinforcing pigments, the latter experiments were repeated with compounds F and H, in which equal loadings of kaolin were substituted for reinforcing black. As Table V shows, kaolin has little reinforcing ability in the present compounds. In Figure 4 the data for compound F show that loss of unsaturation with increasing amounts of combined sulfur is not altered by the presence of this pigment. The same conclusions apply to 45 parts

TABLE IV

AMOUNT OF COMBINED SULFUR AT VARIOUS TIMES OF CURE

Time of cure (min.)	Grams combined sulfur per 100 grams rubber								
	B	C	D	E	F	G	H	I	J
20	—	—	—	—	—	—	0.71	—	—
30	—	—	—	—	—	1.93	—	2.00	1.65
40	—	—	—	—	—	—	1.25	—	—
60	0.34	0.16	2.21	1.67	1.54	2.10	—	2.73	2.41
75	—	—	—	—	—	—	2.48	—	—
90	0.42	0.25	3.46	3.12	2.43	2.98	—	3.02	2.74
120	0.46	0.32	5.12	4.38	3.57	—	3.01	—	—

TABLE V

STRESS-STRAIN DATA OF COMPOUNDS STUDIED

Compound	Cure (min.)	Tensile strength (lbs./sq. in.)	Elongation at break (per cent)	Modulus at 400 per cent (lbs./sq. in.)	Hardness
D	60	3140	550	1800	60
	90	3880	540	2400	63
	120	3900	510	2780	66
F	60	1780	630	610	50
	90	2750	650	850	52
	120	2920	670	870	54
G	30	4370	620	1990	63
	60	4500	560	2760	70
	90	4370	500	2960	72
H	20	2210	660	640	50
	40	3560	670	880	55
	75	3380	650	930	58
I	30	3100	720	400	54
	60	3440	680	530	55
	90	3370	670	520	56
J	20	4070	650	1710	60
	40	4530	580	2500	65
	75	4360	520	2970	68

of clay in a typical tread stock (compound H), as shown in Figure 5. Accordingly, the present data indicate that nonreinforcing fillers have little effect on the course of vulcanization, judged from the combined sulfur-unsaturation values, in contrast to the marked effect of reinforcing fillers noted above.

ASSOCIATION BETWEEN RUBBER AND CARBON BLACK

From the present data it has not been possible to detect any appreciable loss of unsaturation that could be attributed to association of carbon black at the double bonds of the rubber hydrocarbon. Yet there is some body of opinion to the effect that unsaturation is essential for reinforcement. These views are

substantiated in part by the difference in physical behavior of reinforcing pigments in unsaturated natural and synthetic rubber, as contrasted with their behavior in saturated rubberlike polymers of the polyisobutylene (Vistanex) type[12]. The argument can be raised that only a few chemical bonds, of the type suggested above, are essential for reinforcement. The net effect on the total unsaturation would thus be very slight, and possibly beyond detection by present chemical methods. This line of reasoning is somewhat substantiated by the following calculation.

If the assumption is made that only those ethylenic linkages within 3 Å. of the carbon black particle are able to form a true bond with the particle, then it can be shown that the total "saturating" effect of the carbon black is actually quite small. The average diameter of a reinforcing channel black is 300 Å. Assuming the black particle to be spherical, and combination to occur only within 3 Å. of the surface of the particle, then each carbon black particle possesses a "reactive volume" of 8.5×10^5 cubic Å. Since there are about 3.75×10^{16} of the above particles per gram of carbon black, the total "reactive volume" per gram is 3.2×10^{22} cubic Å. From a density of 0.93 for smoked sheet, the total volume of 2 grams of rubber is 2.15×10^{24} cubic Å. Thus, in a compound of 50 parts of black to 100 parts of rubber, only 1.5 per cent of the total rubber hydrocarbon is able to come within the required 3 Å. "reaction distance" of the black particle. Therefore, according to this result, the maximum loss in unsaturation due to carbon black could not exceed 1.5 per cent in the compounds studied. This figure approaches the experimental error in our analytical technique. Accordingly, we must conclude from our data that, if chemical saturation of ethylenic linkages by carbon black does occur, it cannot invoke more than one or two double bonds out of every hundred. According to the above interpretation, loss of unsaturation would be expected to increase with surface area of the black. Carbon blacks with surface areas considerably greater than those studied here are available[15]. According to the above calculation, a black with surface of 300 or 400 M^2 per gram should, if the interpretation is correct, produce effects detectable by our present chemical means. Such experiments are now in progress.

EFFECT OF FILLERS ON VULCANIZATION REACTION

From Figures 4 and 5 it is evident that nonreinforcing fillers have no particular influence on the course of the vulcanization reaction. However, in the presence of reinforcing fillers, as shown in Figures 2 and 3, a marked influence is noted. This is particularly true in the latter case, where we are dealing with accelerated tread stocks. The laboratory rubber tests on compounds G and J (Table V) show them to be well reinforced stocks, yet there is no significant loss in unsaturation with increasing extent of combined sulfur. The concentration of combined sulfur in these stocks is comparable with those of compound I from which filler was omitted and of compound H containing 45 parts of clay. These nonreinforced compounds, in contrast to those containing reinforcing pigments, show a marked loss in unsaturation as cure progresses. Compounds containing reinforcing pigments reach optimum cure with a minimum decrease in unsaturation. In agreement with Hauser's observation[3], they also show maximum stress-strain properties.

The fact that the mechanism of rubber-sulfur combination during vulcanization appears to be markedly altered by the presence of a reinforcing pigment suggests that some portion of the changes induced in rubber stocks by such pigments may be due to the initiation or enhancement of some particular type of sulfur-rubber linkage. Gehman and Field[6] have shown that there is a marked orientation

of rubber molecules in the presence of reinforcing pigments. It may be that, as a consequence of this orientation, certain portions of the rubber molecule are no longer available for reaction with sulfur and, consequently, combination occurs at positions other than those involved in nonreinforced stocks, where this orientation is less pronounced. The formation of this new type of rubber-sulfur linkage in the presence of reinforcing pigments may account for some of the characteristic properties of reinforced rubber stocks. At present we are not able to describe the nature of the sulfur-rubber combination induced by reinforcing pigments, beyond the fact that they occur without loss of unsaturation of the rubber. Although it is undoubtedly true that physical effects play an important role in reinforcement, the possibility that the course of the vulcanization process may be considerably altered by the presence of reinforcing pigments cannot be overlooked.

ACKNOWLEDGMENT

We wish to thank Fred Amon for helpful advice and suggestions during the course of the investigation. We are also indebted to Almon Allard and Harold Offutt for the preparation and physical testing of the rubber stocks, and to Lotus Duerr for valuable aid in preparing the manuscript.

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[21] In Figures 1 to 5, the curves are all displaced slightly so that the percentage unsaturation of the uncured stock is 100 per cent in each case. The deviations from this value, shown in the complete data in Table III, are due to experimental errors in compounding and analysis.

PROPERTIES OF HARD RUBBER

IX. SWELLING IN VARIOUS LIQUIDS

(PART XIII OF SWELLING OF RUBBER) *

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I. INTRODUCTION

An investigation of the swelling of hard rubber was begun with two objects in view:

(1) As part of the wider investigation of the properties of hard rubber, undertaken jointly with the British Electrical and Allied Industries Research Association, to obtain information on the resistance of hard rubber to those liquids with which it may come into contact during use; in view of the scantiness of existing data on this important point, this information should be valuable to users of hard rubber.

(2) As part of the systematic study of the swelling of rubber which has now been in progress for some years, to investigate the swelling properties of hard rubber in general, such as the form of the time-swelling curve, influence of the nature of the swelling liquid, effect of composition and degree of vulcanization of the hard rubber, and effect of temperature.

The present report describes experiments on the swelling of two hard rubbers, containing high and low percentages of combined sulfur, respectively, in 20 liquids, representing a wide variety of chemical types and including certain liquids of practical importance, such as fatty oils, transformer oil, water, alcohol, paraffin, and benzene. The main objects were to examine the dependence of swelling on the chemical nature of the liquid, and to gain some preliminary information on the influence of the combined sulfur content of hard rubber. The absorption of water by hard rubber and other rubbers has been dealt with more fully elsewhere[1], and this liquid was included merely for comparison with others.

An examination of the swelling of a soft vulcanized rubber in various liquids has been described in a previous report[2], to which reference may be made for explanations of the methods used in analyzing the time-swelling curves, and of the terms used in discussing the results (the following changes in nomenclature should be noted: *maximum corrected swelling* and *specific swelling increment* are now called *swelling maximum* and *increment* respectively).

Very little systematic work appears to have been done previously on the swelling of hard rubber and, apart from general statements to the effect that hard rubber is swollen by organic liquids, not much information can be found in the literature.

Boiry[3] examined the swelling of a 65: 35 rubber-sulfur mixing, vulcanized to 23.0 per cent and to 30.9 per cent combined sulfur content, in toluene, xylene, petrol, "petroleum", nitrobenzene, and phenetole, using samples 1 mm. thick. Swelling was measured only after two periods of immersion, so the results do not show the form of the time-swelling curve. Boiry's results, converted to percentage by volume in accordance with standard practice, are given in Table I.

* Reprinted from the *Journal of Rubber Research* of the Research Association of British Rubber Manufacturers, Vol. 10, No. 12, pages 123-145, December 1941.

From these and similar experiments on soft rubber, Boiry concluded that swelling decreased with increasing combined sulfur content, and that the decrease was least rapid with nitrobenzene and most rapid with paraffin hydrocarbons; indeed, the latter were found to have very little swelling action on rubbers containing above 20 per cent of combined sulfur. Boiry made experiments also on "hard rubbers" obtained by vulcanization in solution.

Webster[4] using samples of a 67: 33 rubber-sulfur mixing vulcanized to 29.6 per cent and 30.0 per cent combined sulfur contents, found that the time-swelling curve in benzene had the usual features of the corresponding curve for soft rubber, namely, a rapid initial rise, followed by a very slow uniform increase or increment. The initial rising portion of the curve, however, was more nearly straight than in the soft rubber curve. The amount of liquid absorbed was much less than for soft rubber, but the time taken to reach saturation was longer. The two hard rubber samples differed little in swelling properties.

Porritt and Scott[5] swelled several commercial unloaded and loaded hard rubbers in benzene. The time-swelling curves were similar to those obtained

TABLE I

SWELLING OF HARD RUBBER (BOIRY)

Samples 1 and 2 contained 23.0 per cent and 30.9 per cent combined sulfur, respectively

	Sample 1		Sample 2	
Liquid	After 48 hours	After 7 days	After 48 hours	After 7 days
Toluene	113	113	34	63
Xylene	95	95	16	41
Petrol (sp. gr. 0.73)	10	29	3.1	4.3
Petroleum (sp. gr. 0.80)	5.7	5.7	1.7	2.3
Nitrobenzene	47	74	6.8	15
Phenetole	87	87	18	41

by Webster, except that the increment tended to decrease after very prolonged immersion. The tendency of the initial rising part of the curve to be straight was very pronounced, some curves having a perfectly straight portion or "flat" of considerable length (see Figure (*c*)). The rate of absorption, which was again much slower than for soft rubber, varied more widely between different samples than is the case with soft rubbers. The swelling maximum (calculated on the percentage of rubber-sulfur compound in the case of loaded samples) decreased, and the swelling time increased with increasing combined sulfur content (the results for the unloaded samples are reproduced in Figure (*e*)), but increment did not change appreciably.

Scott[6] tested 65: 35 hard rubbers, some containing zinc oxide and various softeners, in benzene, the results being generally similar to those of Webster and of Porritt and Scott. Among the plain rubber-sulfur samples, swelling maximum again decreased, and swelling time increased with increasing combined sulfur content (see Figure (*e*)).

It will be noted that in Figure (*e*) there is fair agreement between the results of Webster[4], Porritt and Scott[5], and Scott[6]. The increase in swelling time with advancing vulcanization is evident also from Boiry's results (Table I), because saturation of the low-sulfur sample is complete after 48 hours in all liquids except petrol, whereas the high-sulfur sample is nothing like completely saturated after this period.

Ariano[7] stated that an unloaded hard rubber (size of test-piece not mentioned) increased 10 per cent in linear dimensions after 3 days in benzene; for heavily loaded materials the increase was only 1 per cent or less. Swelling was found to reduce the hardness, increase the elasticity (as shown by the rapid disappearance of the indentation produced in the Brinell test), and reduce "fragility".

A swelling test[8] with acetone on one of the hard rubbers (Hl; ash 9 per cent, vulcanization coefficient 41) described in an earlier report[5] gave the following results: swelling maximum 4.2 increment 0.45, swelling time (for test-piece 21×5×6 mm.) about 700.

II. EXPERIMENTAL

1. Hard Rubber Samples

Details of the samples used were as follows:

	Sample A	Sample C
Mixing (rubber: sulfur)	65: 35	72: 28
Period of vulcanization at 155° C (hrs.)	5	3.75
Acetone extract (percentage)	5.0	2.6
Free sulphur (percentage)	3.8	1.1
Combined sulfur (percentage)	31.4	27.2
Vulcanization coefficient	49.5	38.7
Density at 15° C	1.20	1.145

It will be noted that Sample A is vulcanized up to (and apparently beyond) the degree corresponding to the formula C_5H_8S, for which the vulcanization coefficient is 47.1.

2. Liquids

The following liquids were chosen to represent the various chemical types:

Saturated hydrocarbons (paraffins)	Petroleum ether (A.R.; free from aromatic hydrocarbons; b.p. 60°–80° C)
	Paraffin (lamp oil; b.p. 180°–280° C)
	Transformer oil
Hydroaromatic hydrocarbons	Cyclohexane
	Decalin (commercial decahydronaphthol; b.p. 187°–193° C)
Aromatic hydrocarbons	Benzene (A.R.)
	Xylene (commercial "purified")
Organic halogen derivatives	Carbon tetrachloride
	Chlorobenzene
Organic sulfur derivatives	Carbon disulfide
Organic compounds containing polar groups	Alcohol (ethyl; absolute)
	Acetone (A.R.)
	Ethyl acetate
	Glycerine
	Nitrobenzene
	Aniline
	o-Cresol
Fatty oils	Raw linseed oil
	Castor oil
Water	

3. Test Method

A piece of hard rubber measuring 20×19×5.5 mm. was placed in a stoppered bottle, with about 40 cc. of the liquid under examination. The bottle was kept in a thermostat at 34° C, and shielded from light. The test-piece was then

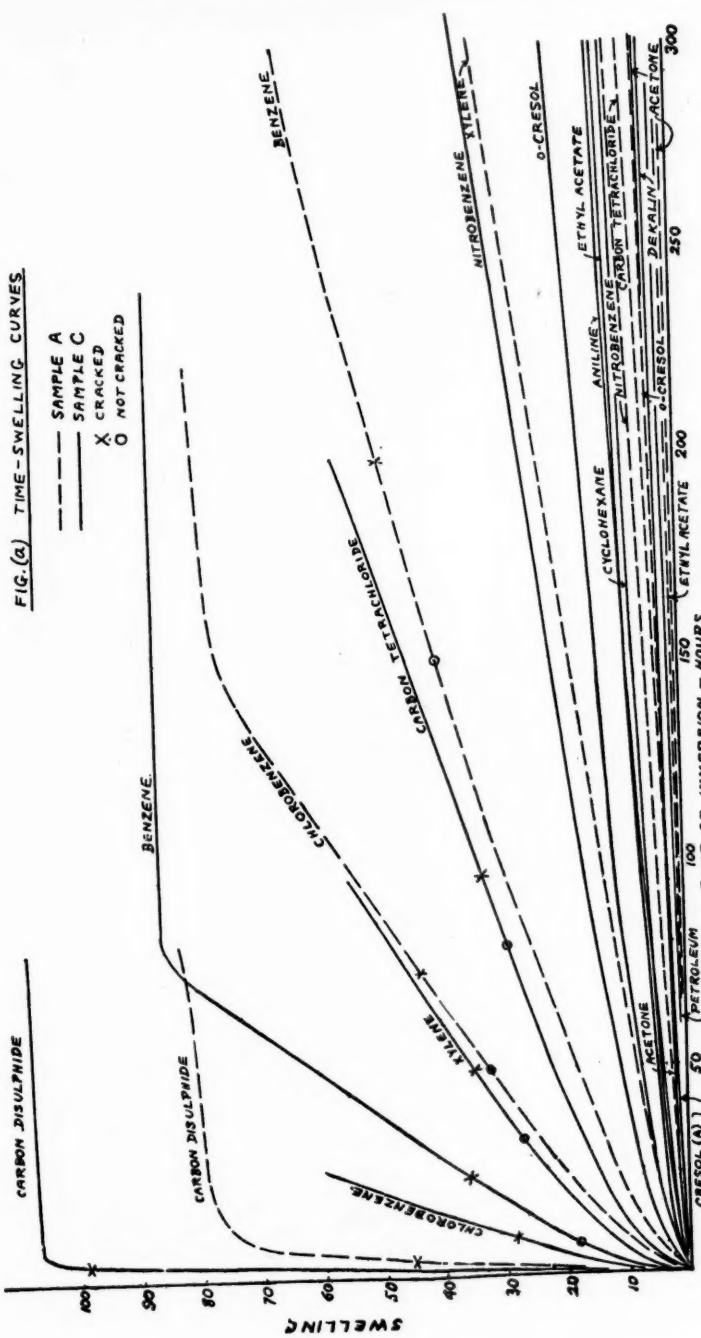
FIG. (a) TIME-SWELLING CURVES.
SAMPLE A
SAMPLE C
X CRACKED
O NOT CRACKED
SWELLING
TIME OF INMERSION - HOURS
CARBON DISULPHIDE
BENZENE
CHLOROBENZENE
CARBON TETRACHLORIDE
TOLUENE
CHLOROBENZENE
CARBON DISULPHIDE
BENZENE
NITROBENZENE
XYLENE
O-CRESOL
ETHYL ACETATE
CYCLOHEXANE
ANILINE
NITROBENZENE
CARBON TETRACHLORIDE
O-CRESOL
DEKALIN
ACETONE
ACETONE
PETROLEUM ETHER
ETHYL ACETATE
CRESOL (A)
CRESOL (A1)
DEKALIN (C)

FIGURE (a).

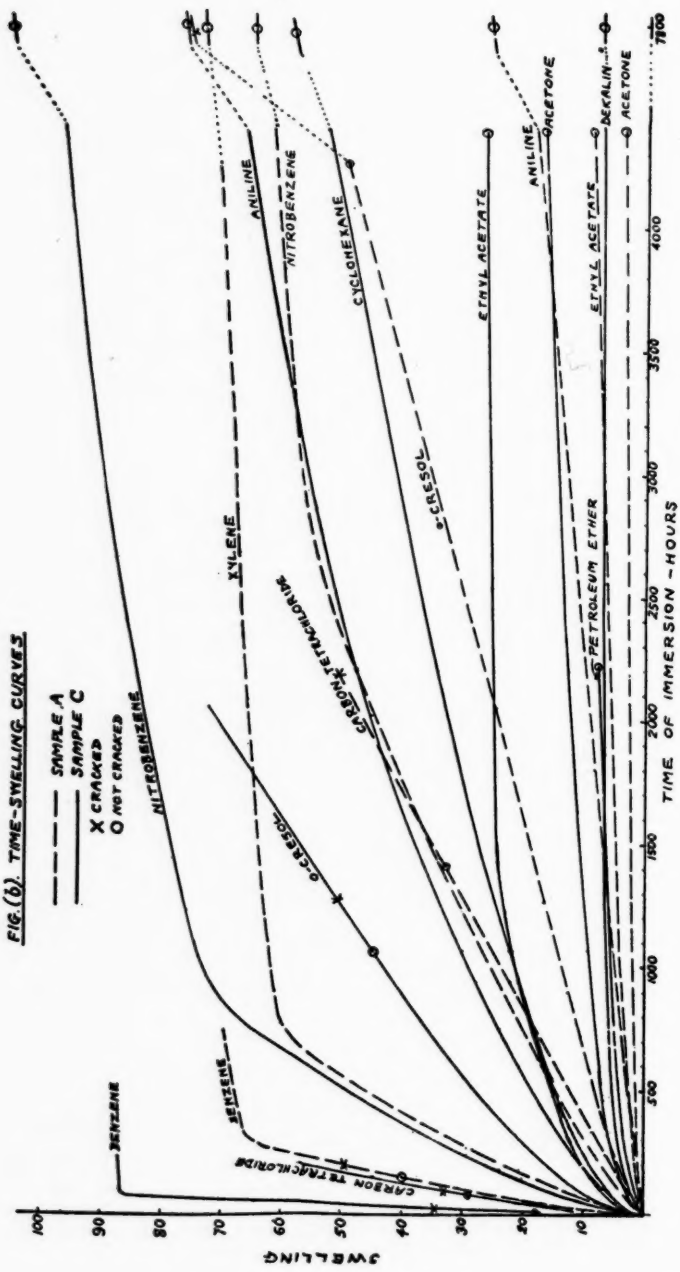
FIG. (b). TIME-SWELLING CURVES
SAMPLE A
SAMPLE C
X CRACKED
O NOT CRACKED
NITROBENZENE
BENZENE
BENZENE
CARBON TETRACHLORIDE
XYLENE
ANILINE
NITROBENZENE
CYCLOHEXANE
CARBON TETRACHLORIDE
o-CRESOL
p-CRESOL
ETHYL ACETATE
ANILINE
ACETONE
PETROLEUM ETHER
ETHYL ACETATE
DEKALIN
ACETONE
SWELLING
TIME OF IMMERSION - HOURS
100
90
80
70
60
50
40
30
20
10
500
1000
1500
2000
2500
3000
3500
4000
4500

FIGURE (b).

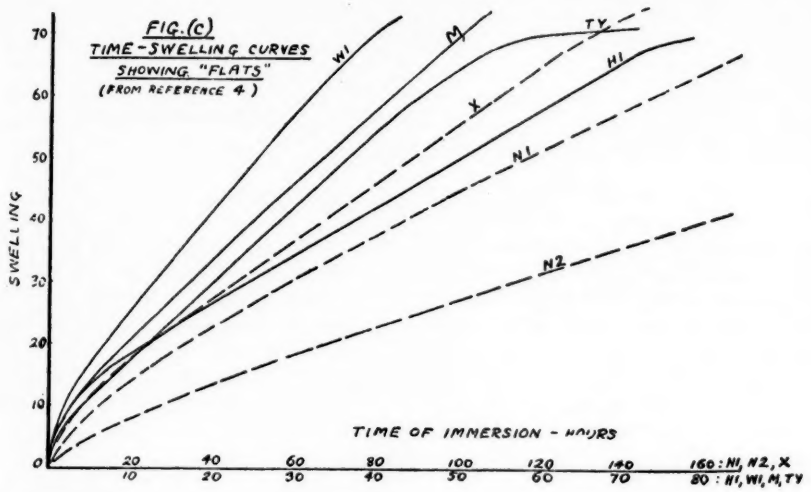

FIGURE (*c*),

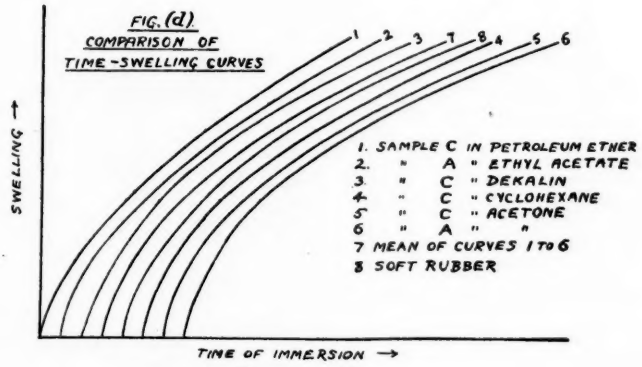
FIG. (d)
COMPARISON OF
TIME-SWELLING CURVES
SWELLING
TIME OF IMMERSION →
1 2 3 7 8 4 5 6
1. SAMPLE C IN PETROLEUM ETHER
2. " A " ETHYL ACETATE
3 " C " DEKALIN
4 " C " CYCLOHEXANE
5 " C " ACETONE
6 " A " "
7 MEAN OF CURVES 1 TO 6
8 SOFT RUBBER

FIGURE (*d*).

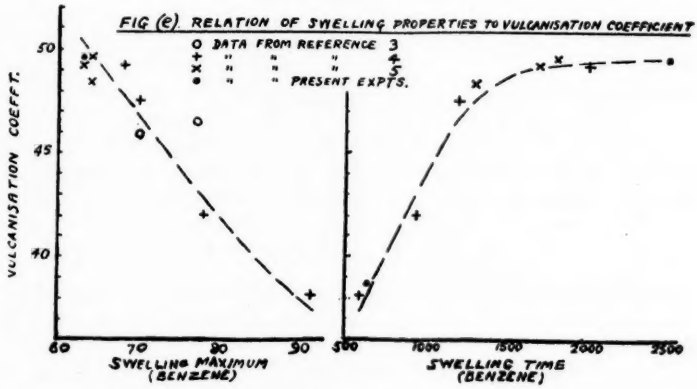

FIGURE (*e*).

weighed after various periods of immersion, ranging from 4 to 4400 hours. Some additional weighings were made after 7800 hours, but these were not accurate because the temperature fell temporarily below 34° C between this and the previous weighing. The swelling after each period was calculated from the increase in weight (*Note:* swelling is defined as the volume of liquid absorbed, expressed as a percentage of the initial volume of the test-piece).

4. Solvent Action of the Liquid

As the test-specimens were usually left in contact with the liquid for very long periods, it was thought advisable to determine whether any dissolution of the hard rubber occurred, especially as the loss of any considerable amount of material by dissolution would render the swelling calculation inaccurate. Accordingly, the liquids left at the end of the long-period tests were evaporated to dryness, and the residual solid matter was weighed and calculated as percentage of the original dry weight of the hard rubber (see Table II).

Table II

Liquid	Hard rubber	Period of immersion (hours)	Extracted matter (percentage)
Petroleum ether	A	2,200	0.2
Petroleum ether	C	2,200	<0.1
Cyclohexane	A	7,800	0.0
Cyclohexane	C	7,800	1.3
Decalin	A	7,800	0.4
Decalin	C	7,800	0.6
Xylene	A	7,800	4.5
Alcohol	A	2,000	0.1
Alcohol	C	7,800	0.4
Acetone	A	4,400	<0.1
Acetone	C	4,400	0.35
Ethyl acetate	A	4,400	0.6
Ethyl acetate	C	7,800	1.1

The results are incomplete because some of the liquids had been discarded before it was decided to determine the extracted matter, and because the high-boiling liquids could not be distilled off without forming tarry or pitch-like substances, which would have vitiated the results.

The extracted matter was always less, and usually much less, than the acetone extract (see above), and as it had the appearance of a normal hard rubber acetone extract, *i.e.*, a mixture of brown resin and crystalline sulfur, it may be concluded that the rubber-sulfur compound itself is insoluble at 34° C in the liquids shown in Table II. It is probable that the same is true of the other liquids, and evidence in support of this is that the initially colorless liquids become only slightly colored during the swelling experiments and that the swollen hard rubber specimens, even after immersion for 7800 hours (nearly a year), preserved their original sharp edges and sowed no signs of surface stickiness.

5. Swelling Results

The curves obtained by plotting swelling against time of immersion (time-swelling curves), excepting those cases where the swelling was zero or extremely small (see below), are shown in Figures (*a*) and (*b*), the former giving the results during the first 300 hours and the latter the complete curves for the

more prolonged experiments. The 7800-hour points have been inserted simply to show that slow absorption of liquid continued beyond the 4400-hour period.

As the amount of soluble matter extracted by the liquid (see Table II) was almost always very small compared with the amount of liquid absorbed, and as it was not known how much of this matter was extracted at any given stage of the experiment, no attempt was made to correct the swelling figures for this extracted matter.

In some experiments, the swelling action of the liquid caused the hard rubber to crack, and these experiments usually had to be abandoned prematurely because the sample became so badly broken that weighing was impossible. Cracking is indicated in Figures (*a*) and (*b*) by a cross at the time when cracking was first noticed, while a circle marks the time when the sample was last known to be uncracked. With carbon disulfide and with sample C in

TABLE III

Liquid	Hard rubber	Swelling after 24 hours	350 hours	2000 hours	4000 hours	7800 hours
Petroleum ether	A	0	—0.1	—0.1(0.1)	—	—
Paraffin	A	—0.1	—0.1	0	—0.1	0
Paraffin	C	0	0.2	0.4	0.5	0.7
Transformer oil	A	—0.1	—0.2	—0.2	—0.2	—0.1
Transformer oil	C	0	—0.1	0	0	0.2
Cyclohexane	A	0	0	0.1	0.4	0.8(0.8)
Decalin	A	0	0.1	0.1	0.1	0.3(0.7)
Alcohol	A	—0.1	—0.1	—0.1(0)	—	—
Alcohol	C	0	0	0	0	0.1(0.5)
Glycerine	A	—0.1	—0.2	—0.2	—0.2	—
Glycerine	C	—0.1	—0.2	—0.2	—0.2	—
Linseed oil	A	0	0	—0.1	—0.1	—
Linseed oil	C	0	0	0	—0.1	—
Castor oil	A	0	—0.1	—0.1	—0.1	—0.1
Castor oil	C	0	—0.1	—0.1	—0.1	—0.1
Water	A	0	0	0.1	0.2	0.2
Water	C	0	0.1	0.2	0.3	0.4

(Figures in parentheses are corrected for soluble matter extracted.)

chlorobenzene, cracking had occurred when the first weighing was taken, so no circle is shown.

In some experiments, no measurable swelling occurred, and indeed there was sometimes a slight loss in weight due to extraction of soluble matter and/or moisture. In some other cases a slight swelling, too small to be shown in Figures (*a*) and (*b*), was produced. The results of these experiments are summarized in Table III.

6. Discussion of Results

(i) *Form of Time-Swelling Curve.*

In many cases the time-swelling curve is broadly similar to that for soft rubber, namely, a relatively quick initial rise or "saturation", followed by a slow uniform (or approximately uniform) increase or "increment". This form of curve is well shown by the following:

Samples A and C in benzene, carbon disulfide, and nitrobenzene;
Sample A in xylene and chlorobenzene;
Sample C in decalin and ethyl acetate.

A similar form of curve has been observed in previous experiments[4, 5, 6].

The following also give curves of this type, though the distinction between the saturation and increment phases is not so clearly marked:

Sample A in acetone and ethyl acetate.
Sample C in acetone, cyclohexane, and petroleum ether.

The curve for A in cresol might be regarded as of this type, though for reasons explained below (paragraph (iv) (*b*)) this is doubtful. The curve for C in aniline shows no substantially straight part that can be identified as the increment. Sample A in carbon tetrachloride gives a type of curve not hitherto observed, namely, an almost perfectly straight line, and A in aniline gives a curve that approaches this type. In the remaining four experiments (in carbon tetrachloride, chlorobenzene, xylene, and cresol) weighings had to be discontinued, owing to cracking, before enough of the curve had been obtained to determine its form.

Although broadly similar to the time-swelling curve for soft rubber, some of the hard rubber curves differ from the latter in having a more or less straight portion or "flat" on the initial saturation part of the curve. This "flat" is most pronounced in cases where considerable swelling occurs, namely, samples A and C in benzene, A in xylene and chlorobenzene, and C in nitrobenzene; the carbon disulfide curves probably show it also, but the number of points on the curves was insufficient to decide this definitely. The existence of a more or less flat portion on the time-swelling curve has been observed in previous experiments with benzene[4, 5, 6], and some of these curves are reproduced in Figure (*c*).

During the normal process of swelling, *i.e.*, absorption of a liquid by a non-crystalline substance which can absorb only a definite limited amount, it is known from theoretical considerations[9] and from experiments that, if the diffusion constant or permeability of the rubber to liquid remains constant, the rate of absorption decreases continuously. The existence of a "flat" *i.e.*, a constant rate of absorption, means that this decrease is being counterbalanced by some other factor tending to increase the rate of absorption as swelling proceeds. Now it is known that the absorption of liquids by hard rubber is extremely slow or, in other words, the diffusion constant is very low and, therefore, it is probable that the diffusion constant increases when the rubber is swollen by absorption of a liquid and so rendered more readily permeable. This would explain why "flats" are most pronounced when considerable swelling occurs, and are not observed when the swelling is small.

Further evidence in support of this explanation is that increase in the diffusion constant during swelling is the more marked, the lower its initial value. This can be shown by calculating the swelling time from various parts of the time-swelling curve, *i.e.*, using various values of k (k is approximately the ratio of swelling to swelling maximum; for precise explanation see Scott[2]). It must be noted that swelling times are calculated by comparison with a standard curve relating to soft rubber. As it is not known to what extent the shape of this curve depends on changes in diffusion constant due to swelling, it is obvious that comparison with the curves for hard rubber cannot show precisely how the diffusion constant of the letter changes during swelling. However, unless the diffusion constant of soft rubber decreases during swelling, which seems highly improbable, the conclusion drawn from the present discussion remains valid.

The swelling for a small value of k (early part of the curve) depends mainly on the initial diffusion constant, whereas that for a high k value (upper part of the curve near the maximum) depends mainly on the diffusion constant of the swollen material. A decrease in swelling time with increase in k, therefore,

implies that the diffusion constant increases as swelling proceeds. Table IV shows the swelling times for $k=0.1$ and $k=0.7$, and also the ratio of these times for benzene and nitrobenzene, which are the only liquids for which adequate data are available, and also for some previous experiments[5, 6]. The results show clearly that hard rubbers with the lowest diffusion constants, *i.e.*, highest swelling times, usually show the greatest increase in diffusion constant during swelling, *i.e.*, lowest values of $T_{0.7}/T_{0.1}$.

Another factor which may tend to accentualte the "flat" on the time-swelling curve is the cracking which often occurs when the swelling is large. Cracking increases the surface exposed to the liquid and therefore accelerates absorption.

TABLE IV

Hard rubber	Liquid	Swelling time (T) $k=0.1$	Swelling time (T) $k=0.7$	$T_{0.7}/T_{0.1}$
A.	Nitrobenzene	51,000	17,000	0.33
C.	Nitrobenzene	7,000	4,700	0.67
A.	Benzene	3,500	1,700	0.49
C.	Benzene	700	450	0.65
N2.*	Benzene	5,700	2,200	0.39
N1.	Benzene	2,800	1,300	0.46
X.	Benzene	2,000	1,100	0.55
W2.	Benzene	1,100	680	0.62
TY.	Benzene	950	410	0.43
M.	Benzene	800	500	0.63
R1.	Benzene	800	470	0.59
R5.	Benzene	590	450	0.76
W1.	Benzene	480	350	0.73
22†	Benzene	9,000	3,600	0.40
15	Benzene	4,800	1,900	0.40
23	Benzene	3,900	1,900	0.49
18	Benzene	2,600	1,450	0.56
19 and 20	Benzene	2,400	1,250	0.52
17	Benzene	1,150	760	0.66
21	Benzene	850	720	0.85

* See reference[4]. † See reference[5].

As the time-swelling curves for liquids with a strong swelling action differ from those for liquids with a weak swelling action, apparently owing to the influence of liquid absorption on the diffusion constant, it is evident that, with hard rubber, there is no standard or normal type of curve applicable to all liquids, as appears to be the case with soft rubber[2]. Nevertheless, when the swelling is small, say, less than 10 per cent, the absorption curves, or to be precise, the "corrected time-swelling curves" as defined by Scott[2], for hard rubbers in different liquids are all about the same shape and similar to the standard curve for soft rubber. This is shown in Figure (*d*), where hard rubber curves are compared with a standard soft rubber curve, all being reduced to the same scales to facilitate comparison.

To see whether the "flat" on the time-swelling curve always bears a fixed geometrical relation to the whole curve, the intercept cut off on the swelling axis by producing the "flat" backwards was measured, and expressed as a fraction of the swelling maximum (see Table V, which includes also data from previous work).

Excepting one or two low figures, most of the values lie around 0.15, showing that the curves as a whole tend towards a uniform geometrical shape.

(ii) *Swelling Constants.*

It has been intended to analyze all the time-swelling curves so as to tabulate the results for convenient discussion in terms of the three constants, swelling maximum, swelling time, and increment but, for the reasons mentioned in the preceding paragraph, this proved to be impossible in some cases. The constants, so far as they could be determined, are given in Table VI. It must be remembered that the loss of a little soluble matter, referred to above, makes the swelling maximum rather low, but not to an extent substantially greater than the experimental error. The increments also may be rendered low owing to the gradual loss of soluble matter.

In those cases where the swelling was extremely small (see Table III) the letters V.S. (very small) have been inserted under swelling maximum. All that

TABLE V

Experiment	Intercept / Swelling maximum	
A in benzene	0.15	
C in benzene	0.155	
A in nitrobenzene	0.13 ±	
C in nitrobenzene	0.16 ±	
A in chlorobenzene	0.13	
65:35 in benzene	0.16 ±	(from reference[4])
H1 in benzene	0.17	(from reference[5]; see Figure (*c*))
N1 in benzene	0.16	
N2 in benzene	0.09	
X in benzene	0.11	
W1 in benzene	0.14	
M in benzene	0.12	
TY in benzene	0.11 ±	

can usually be deduced in such cases is an approximate maximum limit for the increment.

In some experiments, results (marked F) have been calculated on the assumption that the observed straight part of the curve is the flat and not the increment. The flat was extrapolated back to the swelling axis and the swelling maximum calculated from the intercept by using the factor of 0.15 deduced above. This method is undoubtedly the correct one for C in xylene. In other cases, namely, C in carbon tetrachloride, and A and C in cresol, it is not obvious whether the straight part of the curve is the flat or the increment, and results calculated in both ways are therefore given. From a further consideration of the results (see paragraphs (iv), (*a*), (*b*) and (*c*)), it is thought that the figures marked F are the more probable.

Where the time-swelling curve shows a flat, and thus differs in shape from the standard soft rubber curve, the swelling time, calculated in the usual way by comparison with the latter, would obviously vary according to the part of the curve used in the calculation (the figures in Table 4 illustrate this point). In such cases the swelling time has been determined only from the "half-value period" or time taken for the swelling to reach half of its saturation value (in the standard nomenclature[2] this means using $k=0.5$). Figures so calculated are marked H, and are to be regarded merely as approximate indications of the time constant of the swelling process.

Only minimum figures could be given for C in chlorobenzene, owing to the incompleteness of the curve obtained. No figures could be given for aniline or for A in carbon tetrachloride, because these gave abnormal curves.

TABLE VI

Liquid	Hard rubber	Swelling maximum (S)	Swelling time (T)	Increment (I)
Petroleum ether	A	0	—	0
Petroleum ether	C	3.6	3,400	(0.2)
Paraffin	A	0	—	0
Paraffin	C	V.S.(?0.3)	—	<0.01(?0.005)
Transformer oil	A	0	—	0
Transformer oil	C	V.S.	—	<0.003
Cyclohexane	A	V.S.	—	<0.01
Cyclohexane	C	9	1,600	1.0—
Decalin	A	V.S.	—	<0.004
Decalin	C	6.3	3,400	0.025
Benzene	A	64	2,500 H	0.85—
Benzene	C	86	650 H	0.8
Xylene	A	56	5,900 H	0.3—
Xylene	C	90 F	1,600 FH	?
Carbon tetrachloride .	A	?	?	?
Carbon tetrachloride .	C	11 73 F	(170) (2,500) F	23 ? F
Chlorobenzene	A	71	(1,350) H	(3)
Chlorobenzene	C	>60 *	>260 *	?
Carbon disulfide	A	77	70 H	(8)
Carbon disulfide	C	106	(40) H	(2.7)
Alcohol	A	0	—	0
Alcohol	C	V.S.	—	<0.006
Acetone	A	(0.6)	(600)	0.09
Acetone	C	(5)	(1,700)	0.25—
Ethyl acetate	A	2.9	7,200	0.13
Ethyl acetate	C	24	(5,500)	0.06
Glycerine	A and C	0	—	0
Nitrobenzene	A	(52)	(26,000) H	(0.3)
Nitrobenzene	C	63	6,500 H	0.65—
o-Cresol	A	2.8 20 F	(2,000) >35,000 F	1.1 >0.65 F
o-Cresol	C	14 95 F	(1,400) >25,000 F	2.9 ? F
Linseed oil	A and C	0	—	0
Castor oil	A and C	0	—	0
Water	A	V.S.	—	<0.003
Water	C	V.S.	—	<0.005

NOTES: (*a*) A minus sign indicates that the increment gradually decreased with advancing time.
(*b*) Figures in parentheses are approximate only.
(*c*) Figures marked F or H, or with an asterisk are explained in the text.
(*d*) "V.S." denotes very small (probably less than 1).

(iii) *Influence of Combined Sulfur Content of Hard Rubber on its Swelling Properties.*

In every liquid, sample A, with the higher combined sulfur content, swells less than sample C, as indicated by the swelling maximum figures. The difference is most pronounced with liquids which have only a weak swelling action, such as petroleum ether, decalin, cyclohexane, acetone, and ethyl acetate, and is indeed strikingly large in such cases when it is considered that the two samples do not differ greatly in combined sulfur content (A 31.4 per cent; C 27.2 per cent. This decrease in swelling with increase in combined sulfur is in accordance

with previous observations[3, 5, 6], and the results for benzene lie close to the curve relating swelling maximum and vulcanization coefficient deduced from previous observations (see Figure (*e*)). The swelling maximum of 4.2 for a sample with vulcanization coefficient 41 in acetone[8] also agrees satisfactorily with the present results.

The swelling time is usually less for the low-sulfur sample C, indicating that, in general, rubber reaches saturation more quickly the lower its combined sulfur content. This fact has been observed previously[3, 5, 6]. The present values for benzene agree well with the swelling time/vulcanization coefficient curve deduced from these earlier observations (see Figure (*e*)). The swelling time for the sample of vulcanization coefficient 41 in acetone[8], corrected to the size of test-piece used in the present experiments, is about 1000, which is concordant with the present results.

The theory of liquid absorption by rubber developed in connection with water absorption[9] indicates that if rubbers of different swelling maxima but equal diffusion constant are swollen in the same liquid, the swelling time should be greater the higher, the concentration of liquid in the saturated swollen rubber, and experiments on the swelling of suft rubber confirm this[10]. The ratio of swelling time to saturation concentration may therefore be regarded as giving a better idea of the diffusion constant than the swelling time itself, a low value for this ratio indicating a high diffusion constant or rapid penetration of the rubber by the liquid. Table VII gives the values of this ratio, calculated as $T(S+100)/100S$, where S=swelling maximum and T=swelling time.

According to these figures, sample A, with the higher combined sulfur content, is much less readily permeable than sample C by every liquid for which complete data are available.

According to the hypothesis that the swelling increment represents an increase in liquid-absorbing capacity due to depolymerization or disaggregation caused by oxidation[11], the rate of this depolymerization should be measured by the ratio of increment to swelling maximum, because it would be expected that if two rubbers, one of which absorbed more liquid than the other suffer depolymerization at equal rates the resultant increase in swelling, *i.e.*, increment, would be greater for the more absorbent rubber. The ratio of increment to swelling maximum is shown in Table VIII.

In all these cases where figures for both rubbers are available, with the exception of nitrobenzene, the more fully vulcanized sample A gives higher figures than sample C. According to the hypothesis mentioned above, this would indicate that a high combined sulfur content is conducive to degradation under the influence of oxygen.

The earlier experiments already mentioned[5, 6] gave the following values for the increment/swelling maximum ratio (I/S) of unloaded hard rubbers in benzene at 34° C (see Table IX).

These figures are of about the same magnitude as those obtained in the present experiments, and again there is a tendency for the ratio to increase with increasing degree of vulcanization.

(iv) *Relation Between Nature of Liquid and its Swelling Properties.*

(a) *Swelling maximum.*—Considering first the swelling capacity of the liquid, as measured by the swelling maximum, it is evident that, at the temperature used (34° C) liquids consisting essentially of aliphatic hydrocarbons (petroleum ether, paraffin, transformer oil) have no swelling action on sample A and very little or none on sample C. The hydroaromatic hydrocarbons (cyclohexane, decalin) have

a slightly greater swelling action, and aromatic hydrocarbons (benzene, xylene) swell both the hard rubbers considerably, benzene and xylene having about equal swelling capacities.

TABLE VII

Liquid	Viscosity (c.g.s. units)	Ratio of swelling time to saturation concentration	
		Sample A	Sample C
Petroleum ether	0.0032±	—	1000
Cyclohexane	0.007±	—	190
Decalin	0.016±	—	575
Benzene	0.0053	65	14
Xylene	0.0056	165	35
Carbon tetrachloride *	0.0080	—	17± 60±F
Chlorobenzene	0.007±	32±	—
Carbon disulfide	0.0034	1.6	0.8±
Acetone	0.0030	1000	350
Ethyl acetate	0.0038	2600	280
Nitrobenzene	0.0155	750	160
o-Cresol *	>0.035	700 <2100 F	110± >500 F

* Of the alternative figures those marked F (explained in connection with Table VI) are preferred.

TABLE VIII

RATIO OF INCREMENT TO SWELLING MAXIMUM (× 100)

Liquid	Sample A	Sample C
Petroleum ether	—	5.5
Cyclohexane	—	11
Decalin	—	0.4
Benzene	1.3	0.9
Xylene	0.5	—
Chlorobenzene	4	—
Carbon disulfide	10	2.5
Acetone	15	5±
Ethyl acetate	4.5	0.25
Nitrobenzene	0.6±	1.0
o-Cresol *	40 >3 F	20 .? F

* Of the alternative figures those marked F (see Table VI) are preferred.

TABLE IX

Sample	Vulcanization coefficient	I/S × 100	Reference
M	38.1	0.9	4
N1	47.5	1.2	
N2	49.2	1.2	
18	48.4	0.63	5
23	49.2	0.94	
15	49.6	0.84	

Halogen and sulfur derivatives (carbon tetrachloride, chlorobenzene, carbon disulfide) also produce considerable swelling, and are comparable in this respect to the aromatic hydrocarbons.

Considering next liquids containing polar groups, it is seen that aliphatic compounds containing hydroxyl groups (alcohol, glycerine, castor oil) have no

swelling action. Those containing —CO— (carbonyl) or —CO.O— groups (acetone, ethyl acetate), however, exert some swelling action. In view of the small swelling capacity of the lower members of the paraffin hydrocarbon series, exemplified by petroleum ether, the results for these two liquids indicate that the introduction of a —CO— or —CO.O— group does not lower the swelling capacity. The —CO.O— groups in linseed oil are so overshadowed by the long saturated hydrocarbon chains that the results for this liquid can hardly be expected to show what effect these groups have in this type of compound.

Comparing the results for cresol with those for benzene and xylene, it appears that the introduction of a hydroxyl group into an aromatic liquid reduces its swelling action on sample A, though the effect with sample C is doubtful. Introduction of a nitro group slightly reduces the swelling capacity (compare nitrobenzene and benzene). The effect of introducing an amino group cannot be deduced exactly, but comparison of the benzene and aniline curves in Figures (*a*) and (*b*) shows that it does not by any means destroy the swelling capacity.

Fatty oils, as exemplified by linseed oil, appear to have no appreciable swelling action.

It must be emphasized that these results are for a relatively low temperature (34° C). In view of the profound influence of higher temperatures, say, above 70° C, on the physical properties of hard rubber[12], it is highly probable that very different results would be obtained if the liquid were allowed to act at such temperatures. There is evidence of this in the statement of Dunton and Muir[13] that hard rubber is "badly attacked" by 7 days' immersion in "hot" transformer oil, since at 34° C it is practically unaffected by immersion for nearly a year.

It will be of interest now to compare the swelling capacities of the various liquids for hard rubber with their swelling capacities for soft rubber, which are mostly known from previous experiments[2]. Table 10 shows the ratio of the swelling maximum for hard rubber to that for a 95: 5 rubber-sulfur mixing with vulcanization coefficient 4.5. In nearly all cases hard rubber swells much less than soft rubber, as has been observed in previous work[3, 4, 5, 6].

The swelling capacity of hydrocarbon liquids for soft rubber decreases in the order: aromatic, hydroaromatic, aliphatic; thus, a 95: 5 rubber-sulfur vulcanite has swelling maximum 500 in benzene, 460 in cyclohexane, and about 300 in hexane. A similar decrease is observed with hard rubber, but greatly exaggerated, so that the hydroaromatic and aliphatic liquids have very little swelling action. This difference between aromatic and aliphatic liquids was noted by Boiry[3]. Thus, the ratio of the swelling of hard rubber (combined sulfur 23.0 per cent, that is, somewhat less than in sample C) to that of soft rubber (combined sulfur 4.27 per cent, that is, about the same as in the soft rubber referred to in Table X) was as follows:

Toluene	0.185
Xylene	0.165
Petrol	0.07 *
"Petroleum"	0.16

* May be low, as it is not certain whether saturation was reached with the hard rubber.

Figures for the more highly vulcanized hard rubber cannot be given, since Boiry's data do not show whether the experiments were continued until saturation was complete.

It is a striking fact, in view of the powerful swelling action of aliphatic hydrocarbons on raw and soft vulcanized rubber, that, when the rubber is vulcanized

to the stage represented by the formula C_5H_8S, it is completely unaffected by those liquids, at least at temperatures not far removed from atmospheric. The same appears to be true also of linseed oil, which, in view of the preponderance of saturated —CH_2— groups in its composition, might be expected to resemble an aliphatic hydrocarbon in its swelling properties.

The swelling capacities of carbon disulfide and chlorobenzene for hard rubber, relative to those for soft rubber, are about the same as in the case of aromatic hydrocarbons. Of the alternative figures for carbon tetrachloride, the higher one (marked F) seems more in keeping with the anticipated similarity between this liquid and carbon disulfide and chlorobenzene. This conclusion is supported by the following evidence: The smaller figure (0.016) would indicate that, with

TABLE X

RATIO OF SWELLING MAXIMUM TO THAT OF SOFT RUBBER

Liquid	Sample A	Sample C
Petroleum ether	0	0.015
Paraffin	0	0+
Transformer oil (*a*)	0	0+
Cyclohexane	0+	0.02
Decalin	0+	0.012
Benzene	0.125	0.17
Xylene	0.115	0.18
Carbon tetrachloride	?	0.016 0.11 F
Chlorobenzene (*b*)	0.134	>0.11
Carbon disulfide	0.130	0.180
Acetone (*c*)	0.05	0.45
Ethyl acetate (*c*)	0.12	1.0
Nitrobenzene	0.38	0.44
Linseed oil (*d*)	0	0

NOTES: 0 + denotes a very small value.
F has the significance explained in connection with Table VI.
(*a*) Soft rubber has not been tested in transformer oil, but in mineral lubricating oil it gives a swelling maximum of 180[16].
(*b*) Soft rubber figure from Le Blanc and Kröger[14].
(*c*) Soft rubber figures from Flusin[15].
(*d*) Soft rubber figure from Scott[16].

increasing degree of vulcanization, the swelling capacity of carbon tetrachloride decreased as rapidly as that of the aliphatic hydrocarbons. The rapidity of the decrease with the latter results in a marked decrease in swelling capacity, relative to that of benzene, even within the range of combined sulfur contents met with in soft rubbers[2]. Carbon tetrachloride, however, shows no such decrease[2], and this fact is, therefore, evidence against the view that its swelling capacity changes with combined sulfur content in the same way as that of aliphatic hydrocarbons.

With liquids containing polar groups (acetone, ethyl acetate, nitrobenzene) the hard rubber/soft rubber ratio is higher than for the other liquids, at least with sample C. The results for aniline unfortunately do not lend themselves to quantitative treatment, but with sample C swelling after the first 300 hours is actually greater than for a 95: 5 rubber-sulfur vulcanizate[2]. This result, therefore, supports the conclusion that polar liquids have an unusually large swelling action on hard rubber. Boiry's results also point to the same conclusion; his

ratios for hard rubber to soft rubber (combined sulfur 23.0 and 4.27 per cent, respectively) are as follows:

Nitrobenzene	0.44 *
Phenetole (phenylethyl ether)	0.22

* May be low, as it is not certain that the hard rubber was fully saturated.

The present experiments show, therefore, that the influence of increasing combined sulfur content on the swelling of vulcanized rubber varies according to the nature of the liquid. In practically all cases swelling decreases over the whole range from raw rubber to C_5H_8S. The decrease is, however, exceptionally rapid with aliphatic hydrocarbons, whose swelling action becomes very small when the combined sulfur reaches about 25 per cent and vanishes altogether at 32 per cent. Hydroaromatic hydrocarbons apparently show a slightly less rapid decrease; aromatic hydrocarbons and halogen and sulfur derivatives of hydrocarbons show a markedly slower decrease. The decrease is least rapid with liquids containing polar groups. The difference in rate of decrease between different liquids may be so pronounced that the relative swelling capacities of two liquids are reversed on passing from soft rubber to hard rubber. Thus, petroleum either swells soft rubber more than nitrobenzene, but the latter has by far the greater swelling action on hard rubber.

This change in the relative affinities of the rubber for different chemical types of liquids is evidently due to the change in the chemical nature of the rubber.

(b) *Swelling time.*—In general, the swelling times for hard rubber are much greater than those for soft rubber in the same liquids, *i.e.*, hard rubber takes longer to reach saturation (cf. soft rubber figures in the work of Scott[2]; these are not strictly comparable with the present figures because of differences in temperature and size of test-piece, but as the effects of these differences are small and tend to cancel each other, the comparison is not seriously affected). The only exception is carbon disulfide, which saturates hard rubber almost as quickly as soft rubber. This, however, does not mean that the diffusion constant of carbon disulfide in hard rubber is the same as in soft rubber, because, owing to the dependence of swelling time on saturation concentration (see paragraph (iii) above) and the fact that this concentration is much lower in hard rubber than in soft rubber, a hard rubber of low diffusion constant might have the same swelling time as a soft rubber of higher diffusion constant.

With hard rubber there are far greater differences between the swelling times of different liquids than is the case with soft rubber. Thus, taking four liquids which are comparable in swelling maxima, the swelling times relative to that of benzene are:

	Soft rubber	Hard rubber C	Hard rubber A
Carbon disulfide	0.45	0.06	0.03
Benzene	1.0	1.0	1.0
Xylene	1.1	2.5	2.4
Nitrobenzene	4.3	10	10.5

In the swelling of soft rubber it has been found that, in general, the less viscous the liquid, the lower is its swelling time[2]. This relationship does not apply to hard rubber, because acetone and petroleum ether are less viscous than benzene, xylene, and carbon disulfide (see Table VII), yet the former have higher swelling times. It has already been explained in paragraph (iii) that the ratio of swelling time to saturation concentration (T/C ratio) is probably better than the swelling

time itself as an indication of the diffusion constant in the swelling process. From the values of this ratio (Table VII), some of the least viscous liquids, namely, acetone, ethyl acetate, and petroleum ether appear to diffuse most slowly. This can be explained by the influence of the absorbed liquid on the permeability of the rubber to liquid, already referred to in paragraph (i). The three liquids mentioned have only a small swelling action, so that the swelling time represents the rate of diffusion into substantially dry hard rubber, which is very slow. Cyclohexane may be included in this category; the reason for its giving a lower T/C ratio than the less viscous liquids acetone, ethyl acetate, and petroleum ether may be its relatively high increment, which increases the total swelling and so helps to increase the permeability of the rubber.

The fact that carbon disulfide, benzene, xylene, and chlorobenzene, which have about the same viscosities as the above-mentioned liquids, diffuse much more rapidly, and even the highly viscous nitrobenzene diffuses distinctly more quickly, can be ascribed to the stronger swelling action of these liquids, which greatly increases the permeability of the rubber. The figures for carbon tetrachloride in Table VII suggest that it should be included in the category of strongly swelling liquids, in which case the bottom figures for swelling maximum (73) and swelling time (2500) given in Table VI should be accepted.

The high T/C ratio for decalin is due partly to its low swelling capacity and partly to its high viscosity.

The upper set of figures for cresol in Table VII were calculated on the assumption that the swelling maxima for samples A and C were 2.8 and 14, respectively. This would put cresol among the weakly swelling liquids, like acetone, ethyl acetate, and petroleum ether. As cresol is much more viscous than these liquids, its T/C ratio would be expected to be much greater, whereas actually it is less, according to the upper set of figures. The lower set of figures were calculated from swelling maxima of 20 and 95, which put cresol in the same class as nitrobenzene. Being more viscous than the latter, it would be expected to have a higher T/C ratio, as is found to be the case. Although the lower set of figures (and the corresponding figures in Table VI) thus appear more probable, it must be realized that a definite decision on this point is not possible.

The conclusion to be drawn is that, although viscosity or some related property is probably a factor in determining the rate of penetration of hard rubber by a liquid, the permeability of the rubber is so greatly increased by absorption of liquid that the swelling capacity of the liquid is a more important factor.

(c) *Increment.*—In view of the enormous influence of even traces of certain substances on the increment[11] and the fact that the liquids used, although reasonably pure, were not subjected to rigorous purification, the observed increments cannot be relied on as indicating the relative depolymerizing effects of the various liquids.

It may be noted that the upper figures given in Table VI for sample C swelling in carbon tetrachloride give a value of 210 for $I/S \times 100$. As this is very much higher than the corresponding value for any other liquid (cf. Table VIII) and carbon tetrachloride has not been found to give abnormally high increments[2], this fact may be taken as further evidence in favor of accepting the lower set of figures.

(v) *Cracking.*

Examination of Figures (*a*) and (*b*) shows that the occurrence or absence of cracking does not depend solely on the amount of liquid absorbed. Thus,

sample A cracks on absorbing 45 per cent (or perhaps less) of carbon disulfide, but does not crack after absorbing 73 per cent of xylene; sample C can absorb 77 per cent of aniline or 105 per cent of nitrobenzene without cracking, but cracks after absorbing about 30 per cent of benzene, xylene, or carbon tetrachloride.

This observation can be explained in part by the fact that cracking is due to stresses set up by the unequal distension of the rubber during the early stages of swelling, when the absorbed liquid is not uniformly distributed. Thus, of two rubbers containing the same proportion of liquid but in the one case distributed uniformly (as at the swelling maximum), and in the other case non-uniformly (as during the earlier stages), the latter would be the more likely to crack. This explanation is supported by the fact that cracking nearly always occurs during the initial rapid absorption of liquid.

Nevertheless, it is difficult to understand why, for instance, sample A in xylene and C is nitrobenzene (see Figure (*b*)) do not crack, whereas A in benzene and C in cresol do, or why A in carbon tetrachloride cracks whereas A in nitrobenzene and C in aniline do not. It is possible that the influence of swelling on the mechanical properties of hard rubber may depend on the chemical nature of the liquid.

Sample A withstands greater swelling without cracking than does sample C, as is shown in Table XI which gives the approximate swelling at which cracking commences.

TABLE XI

Liquid	Sample A	Sample C
Benzene	45	30
Xylene	>73	30
Carbon tetrachloride	43	30
Chlorobenzene	38	<28
Cresol	60	48

7. Mechanical Properties of Swollen Hard Rubber

Hard rubber becomes much softer after immersion in liquids that have a strong swelling action, an effect that has been observed previously[4, 7]. Thus, samples that have been swollen in nitrobenzene have much the same rigidity as the carbon black rubbers used for shoe solings. Unlike the latter, however, swollen hard rubber seems almost perfectly elastic so, when released after being bent, it returns immediately to its original form. Ariano[7] noticed that hard rubber became more elastic on swelling, and the same effect is found in the swelling of soft rubber. Swollen hard rubber is relatively brittle, however, as it cannot be bent far without breaking. The cracking that often occurs during swelling is further evidence of this, as the strains caused by swellings are never large.

III. SUMMARY AND CONCLUSIONS

1. Literature on the swelling of hard rubber is reviewed (Section I).

2. Experiments are described on the swelling of two hard rubbers, with high and low combined sulfur contents, respectively, in a representative selection of 20 liquids at 34° C (Section II).

3. It is shown that at 34° C hard rubber is virtually insoluble in common organic liquids, but that it absorbs considerable amounts (up to 100 per cent) of some liquids, although unaffected by others (II, 4 and 5).

4. The time-swelling curves of hard rubber are usually similar to those of soft rubber, except when the swelling is large; in these cases the absorbed liquid apparently increases the permeability of the rubber and so alters the shape of the curve (II, 6(i)).

5. The swelling properties (swelling maximum, swelling time, increment) of the two hard rubbers in the 20 liquids, so far as they could be determined, are tabulated (Table VI) and discussed in relation to the degree of vulcanization of the rubber and the chemical and physical properties of the liquid, the following being the main conclusions:

(*a*) With increasing combined sulfur content, the amount of liquid absorbed decreases, but the time required to reach saturation usually increases (II, 6(iii)).

(*b*) The swelling action of practically all liquids decreases, as the degree of vulcanization increases, over the whole range from raw rubber to hard rubber, but the rate of decrease varies according to the chemical nature of the liquid. In consequence of this, aromatic hydrocarbons, halogenated hydrocarbons, and carbon disulfide have the strongest swelling action on hard rubber, whereas hydroaromatic hydrocarbons and especially paraffin hydrocarbons (and apparently fatty oils also) have very little or none; polar compounds are intermediate. An important result is that at 34° C hard rubber vulcanized to the stage corresponding to C_5H_8S is quite unaffected by paraffin hydrocarbons and linseed oil (II, 6(iv) (*a*)).

(*c*) There is no simple relation between the viscosity of a liquid and the time required to reach saturation, as with soft rubber, because strongly swelling liquids are absorbed relatively more quickly than weakly swelling liquids, apparently because they increase the permeability of the rubber (II, 6(iv) (*b*)).

6. Liquids with a strong swelling action often, but not always, cause hard rubber to crack; a high combined sulfur content seems to make the rubber more resistant to this cracking (II, 6(v)). Notes are added on the mechanical properties of swollen hard rubber (II, 7).

7. The present results indicate that hard rubber intended to resist the action of organic liquids at temperatures not far above atmospheric should be vulcanized as fully as is consistent with its having the other properties required because, by so doing, its resistance to swelling and cracking is increased. The only possible objection to this at present evident is that a high degree of vulcanization may accentuate the very slow increase in swelling (increment) which continues indefinitely after saturation has been reached, although from the present results (Table VI) this does not appear to be usual, so that the objection does not seem serious.

8. It is recommended that, in future swelling tests on hard rubber, the test-pieces be thinner (1 or 2 mm.) than at present (5.5 mm.), as this would greatly accelerate absorption. By so doing, the experiments would be shortened and an interpretation of the time-swelling curves facilitated, because the distinction between the saturation and increment phases would be clearer. A lower test temperature might be advantageous also, since it would reduce the increment.

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THE VISCOSITY OF PRESERVED AND CONCENTRATED LATEX

III. RELATIONSHIP OF VISCOSITY TO TEMPERATURE AND DRY-RUBBER CONTENT *

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The purpose of this paper is to deduce, from data given by Rhodes[1] on the viscosity of latices and of latex-water mixtures at different temperatures, mathematical formulas by which the observations may be succinctly described. These will serve as a convenient means for interpolation and for the deduction of quantitative estimates of the changes in the viscosity of latex with temperature and dry rubber content (d.r.c.); and may facilitate comparison with the variations in viscosity of other substances and with theories or hypotheses.

DATA

The data give the viscosities at temperatures from 15 to 85° C of 14 samples of field latex of 32.5 to 39.3 per cent dry rubber content, preserved with liquid ammonia to an NH_3 content of 0.43 to 1.0 per cent, and of two centrifuged concentrates, and six mixtures of each with water, giving 14 suspensions varying from 30 to 59 per cent d.r.c. The NH_3 contents of the original concentrates were 0.9 and 0.43 per cent. For purposes of reference, the field latices are numbered F_1 to F_3 and 1 to 11, and the two series of concentrates and concentrate-water mixtures are referred to as F_5 and F_6. The data for the F series have been published by Rhodes[1], in whose paper the figures of corresponding number show graphs of the viscosity in centipoises as a function of the temperature (in degrees centigrade). The data for latices 1 to 11 have not previously been published.

Viscosity determinations were made in a Höppler viscometer equipped with an "ultra-thermostat". Before being put into the viscometer, all samples were clarified by centrifuging for 10 minutes at 2000 revolutions per minute, and decanting from the settled sludge[2].

Each "observation" was recorded as the mean of two times of fall of either Ball No. 1 or No. 2, supplied with the viscometer. Since, however, successive observations of any one series through a range of temperatures appear to be correlated, the experiments cannot be considered to have been replicated in the usual statistical sense, and valid experimental errors cannot be calculated. Differences between duplicate fall-times indicate that, for most of the data, the standard error of a single observation cannot be less than 0.4 per cent (in logarithms $\pm$ .002); miscellaneous evidence suggests that the total random errors may be not much greater. Concerning possible systematic (instrumental) errors, we have little information. Comparison with data given by other workers suggests that observations at viscosities less than 20 cp. may be fairly reliable; but miscellaneous evidence suggests that observations greater than 30 cp. may be unreliable, and those between 20 and 30 cp. doubtful. This condition arises,

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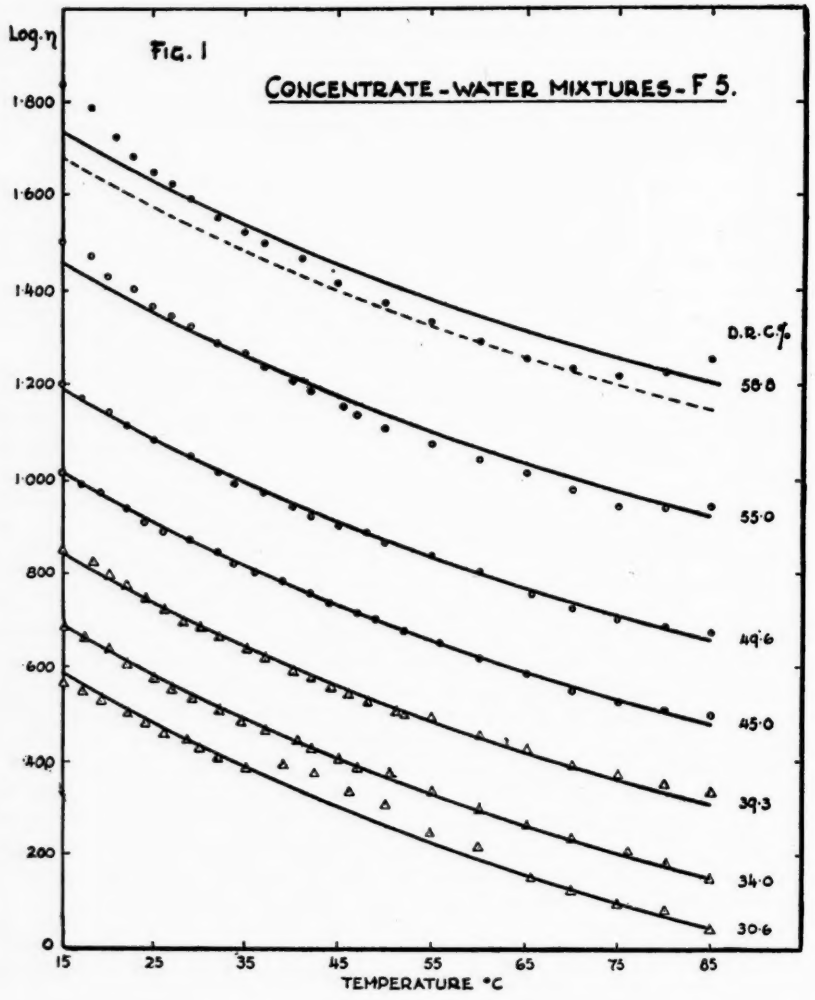
presumably, because observations with the Höppler viscometer take no account of the rate of shear.

Computations in this paper are based on estimates of viscosities computed to 0.01 cp. Therefore they may not check exactly with computations repeated on the published figures, which were given only to 0.1 cp.[3]

VARIATION OF VISCOSITY WITH TEMPERATURE AND DRY RUBBER CONTENT

Figures 1 to 6 show the logarithms of viscosities graphed against temperatures. The observed points indicate curves which are substantially parallel except for concentrates with viscosities greater than 20 cp. ($\log\eta$ greater than 1.3). The



variation of viscosity with temperature and d.r.c. may therefore be described, to a first approximation, by an equation of the form:

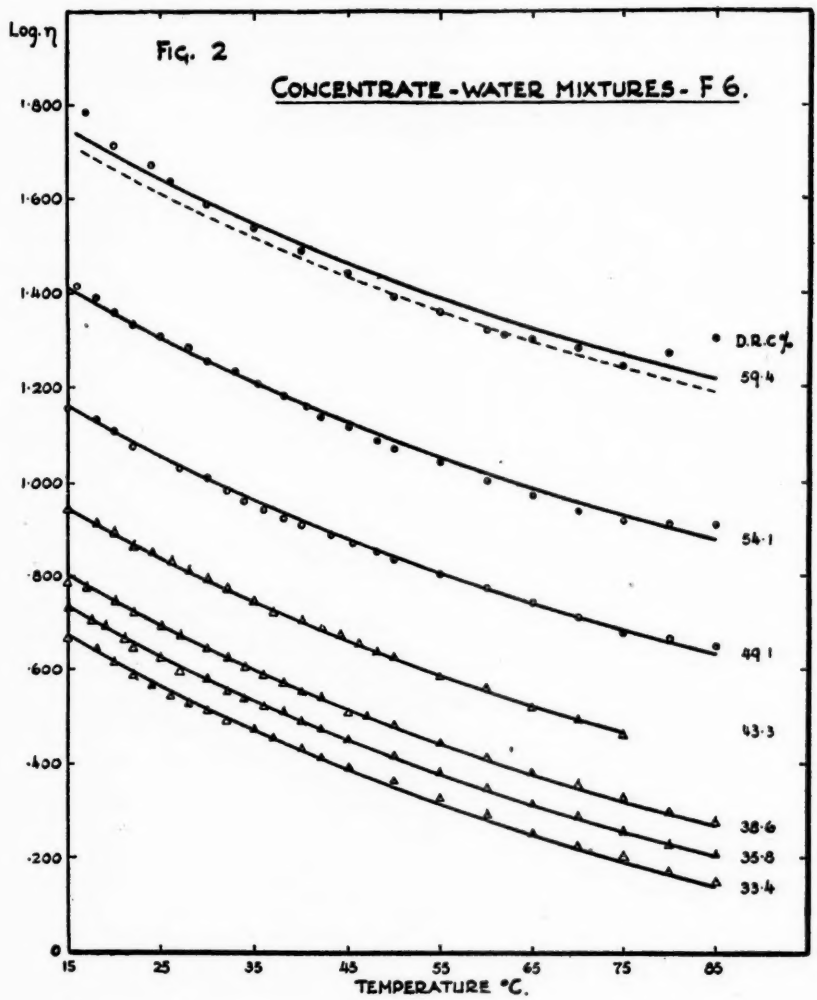
$$\log\eta = f_1(t) + f_2(\phi) \tag{1}$$

where $f_1(t)$ is some function of temperature, and $f_2(\phi)$ is a function of d.r.c. and other latex characteristics, such as serum solids.

The curves fitted to each series in Figures 1 to 6 are given by:

$$\log\eta = \log\eta_w + m \tag{2}$$

where η_w is the viscosity of water, and m is a constant fitted for each latex (or concentrate-water mixture), and is equal to the average of log (η_s/η_w), where η_s is the observed viscosity of the suspension (latex or concentrate-water mixture) at each temperature.



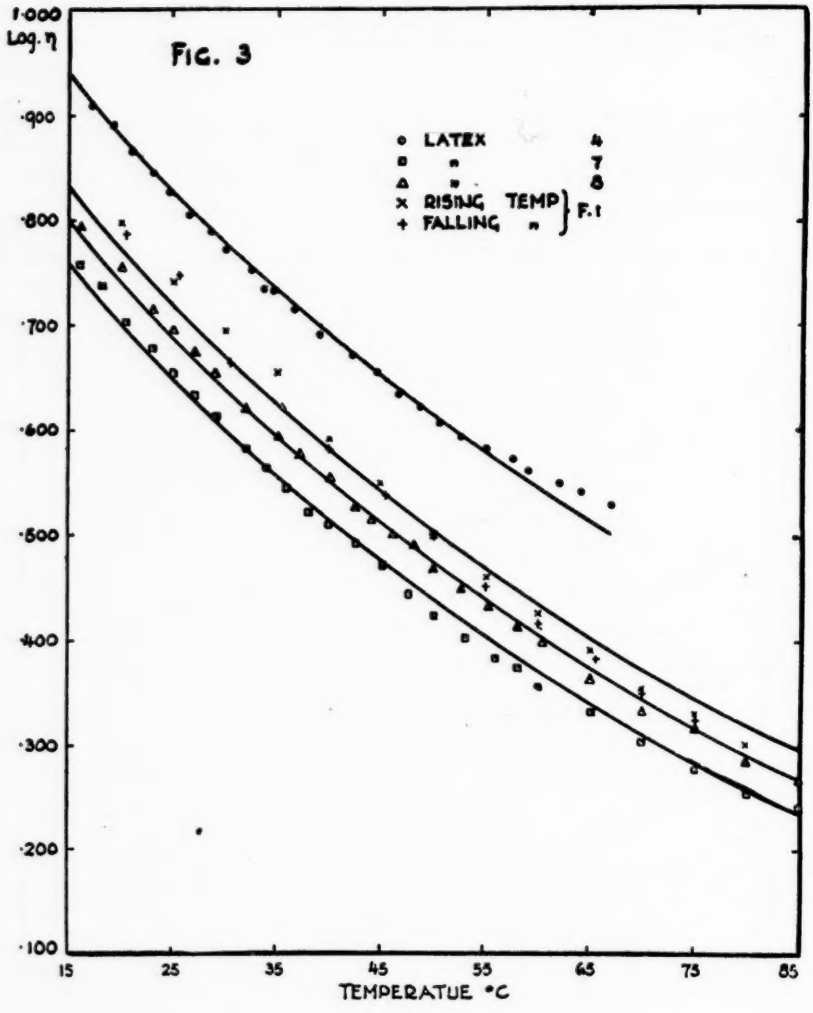


FIG. 3
1·000
Log. η
·900
·800
·700
·600
·500
·400
·300
·200
·100
LATEX 4
" 7
" 8
RISING TEMP } F.1
FALLING "
15
25
35
45
55
65
75
85
TEMPERATUE °C

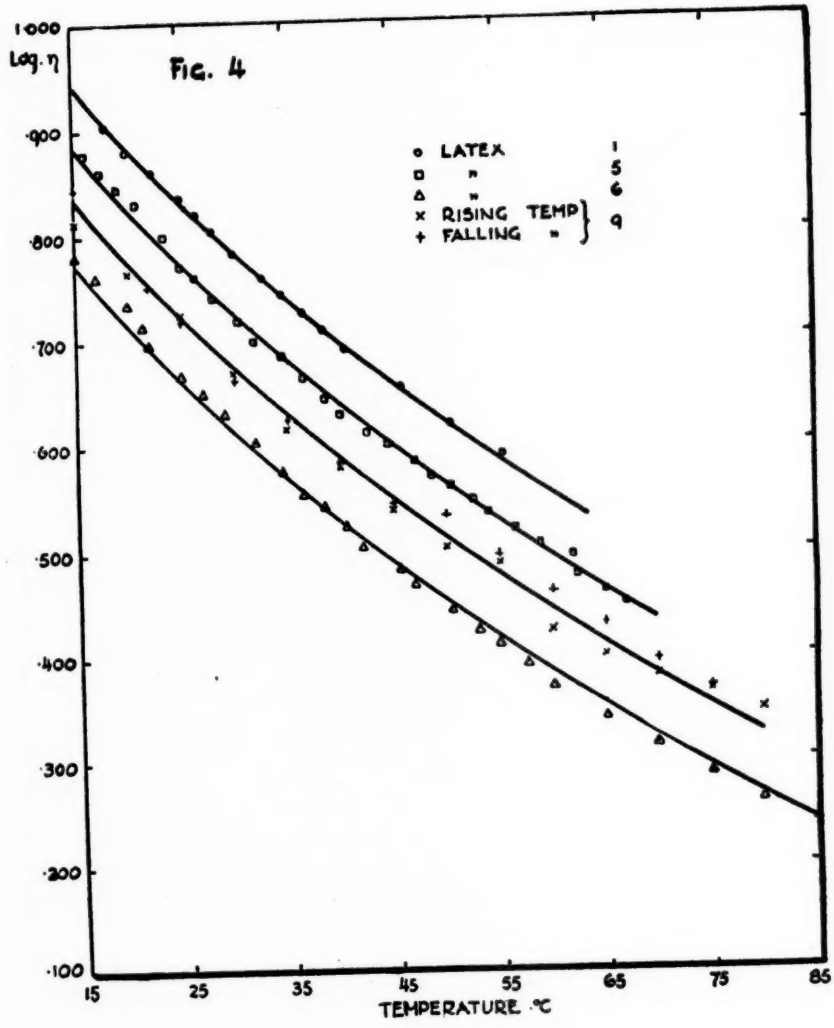


Fig. 4
Log. η
1·000
·900
·800
·700
·600
·500
·400
·300
·200
·100
o LATEX 1
□ " 5
△ " 6
× RISING TEMP } 9
+ FALLING " }
15
25
35
45
55
65
75
85
TEMPERATURE °C

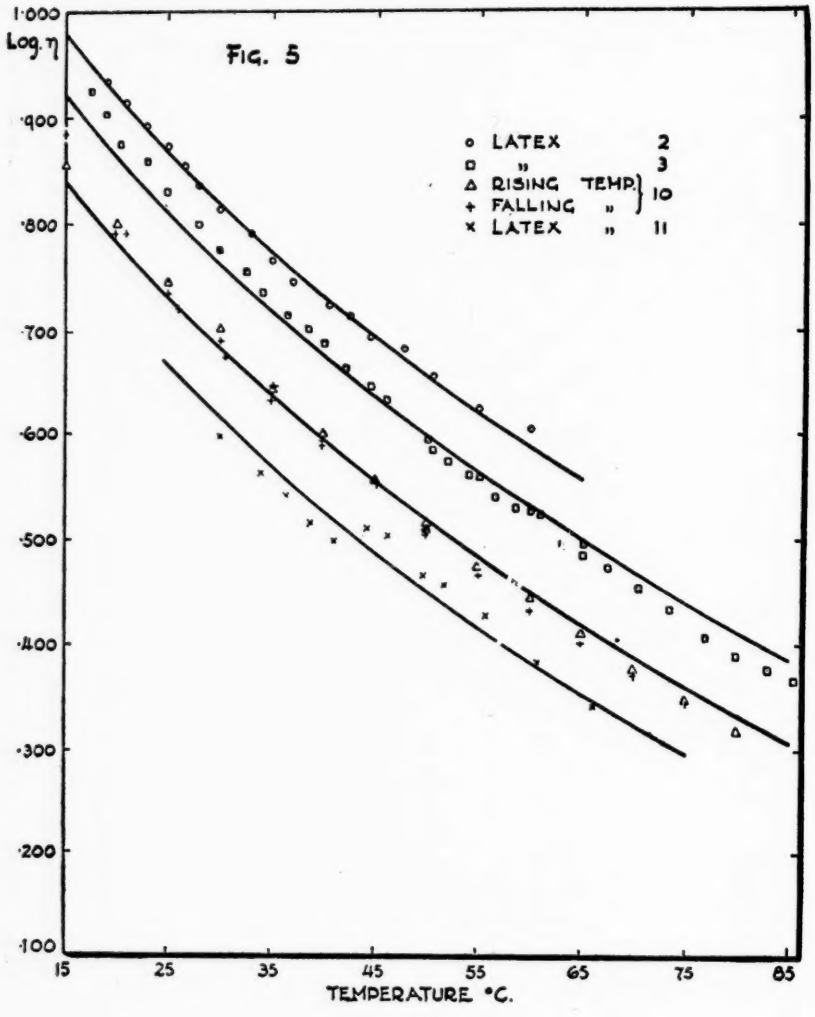


FIG. 5
Log. η
1·000
·900
·800
·700
·600
·500
·400
·300
·200
·100
15
25
35
45
55
65
75
85
TEMPERATURE °C.
o LATEX 2
□ " 3
△ RISING TEMP. } 10
+ FALLING " }
× LATEX " 11

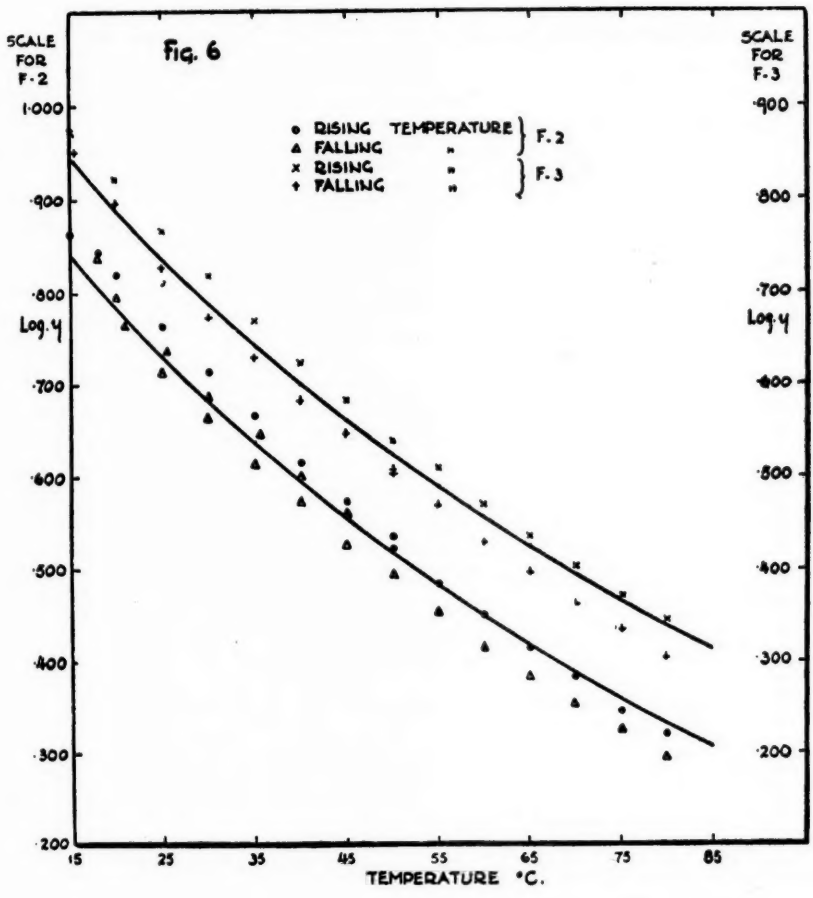


Fig. 6
SCALE FOR F·2
SCALE FOR F·3
RISING TEMPERATURE } F.2
FALLING "
RISING " } F.3
FALLING "
Log.η
1·000
·900
·800
·700
·600
·500
·400
·300
·200
15
25
35
45
55
65
75
85
TEMPERATURE °C.

For five of the field latices, *viz.*, F_1, F_2, F_3, 3 and 10, the rate of change of viscosity with temperature seems to be greater than shown by the curve for water. The deviation is, however, not great, and until we have data observed at varying and known rates of shear, and for latices of known serum solids, it is scarcely worth while to examine these deviations in more detail. Since observations of $\log\eta_s$ greater than 1.3 are suspect, it is possible that the departure from the fitted curves of those relating to the 58.8 and 59.6 per cent concentrates is artificial; curves given by (2) with m estimated from (4) below, shown as dotted lines in Figures 1 and 2, may be more nearly correct than the observations.

Equation (1) may, therefore, be elaborated by expressing $\log\eta_w$ as a function of temperature, and m as a function of d.r.c.

No fundamental formula for the viscosity-temperature curve of water is known. For estimation in a given range, a cubic polynomial seems to be as accurate as, and is more convenient for computation than, the numerous other formulas which have been suggested. The best fitting equation for $\log_{10}\eta_w$ as a third order polynomial of t in ° C from 15 to 80° C, for viscosity in centipoises, is:

$$\log_{10}\eta_w = .2538 - .014394t + .00010198t^2 - .00000039604t^3 \quad . \quad . \quad . \quad . \tag{3}$$

$$= -.0485 - .010037(t-25) + .000072278(t-25)^2 - .00000039604(t-25)^3 \quad . \quad . \quad . \quad . \tag{3a}$$

From 14 to 81° C, this equation gives values of $\log\eta_w$ differing from the logarithms of the values in Critical Tables by less than .001 (estimates of η_w differing by less than 0.2 per cent).

Figure 7[4] shows the values of m for the concentrate-water mixtures (F_5 and F_6) graphed against r_w=d.r.c./(100−d.r.c.)=ratio rubber: serum by weight. Excluding, because of their suspected inaccuracy, the values for concentrates of d.r.c. greater than 58 per cent (r_w greater than 1.4), the regression of m or r_w is found to be:

$$m = .0621 + 1.0905r_w \pm .00755 \pm .00932 \tag{4}$$

For the ammoniated field latices (Figure 8[4]) the regression is:

$$m = .062 + 1.3024r_w \pm .0448 \pm .0795 \tag{5}$$

The corresponding equation fitted to viscosities of 924 samples of field latex reported in Part I, Table I, but excluding samples with less than 28 per cent d.r.c., is (*cf.* Equation 3 and Table IVa of Part I):

$$\log(\eta/\eta_w) = .253 + 1.0173r \pm .00415 \tag{6}$$

and is shown as a broken line in Figure 8[4]. The difference between these and the latices reported above may be due in part to the different methods of clarifying the two series of latices, the older lot having been sieved, while the fourteen discussed above were centrifuged; it may also be due to the source of latex, all the 14 samples having been obtained from the smallholding adjacent to the Institute.

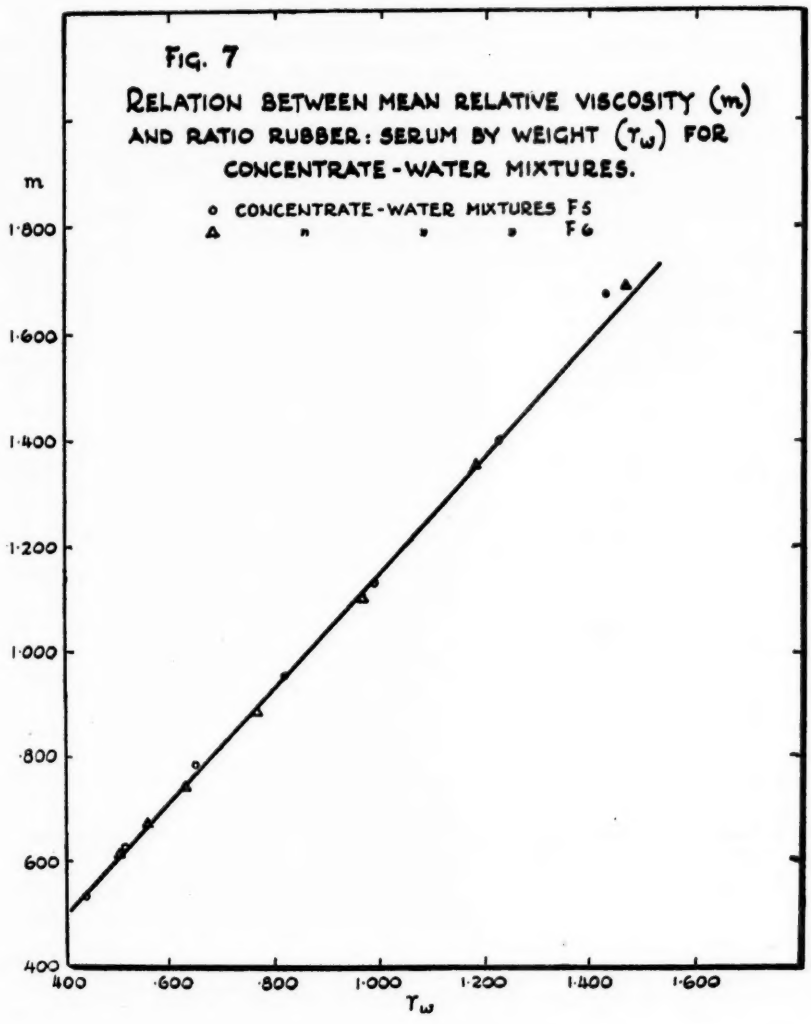


FIG. 7
RELATION BETWEEN MEAN RELATIVE VISCOSITY (m) AND RATIO RUBBER: SERUM BY WEIGHT (r_w) FOR CONCENTRATE-WATER MIXTURES.
o CONCENTRATE-WATER MIXTURES F5
Δ " " " F6
m
1·800
1·600
1·400
1·200
1·000
·800
600
400
400
·600
·800
1·000
1·200
1·400
1·600
r_w

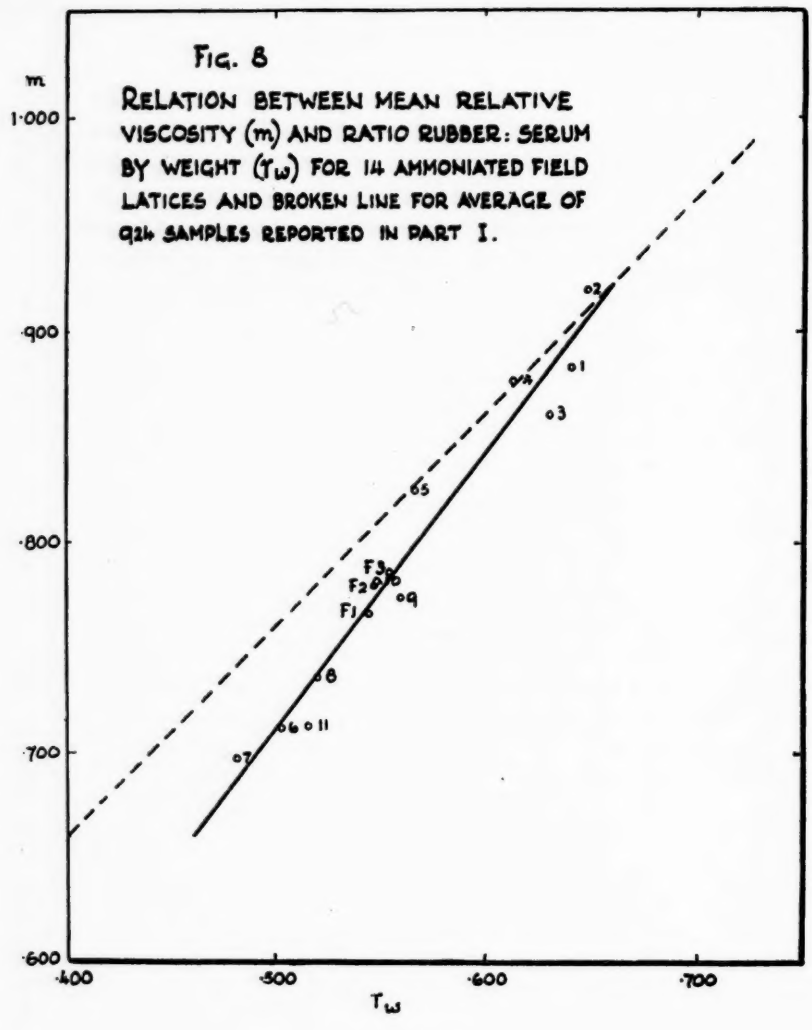


FIG. 8

RELATION BETWEEN MEAN RELATIVE VISCOSITY (m) AND RATIO RUBBER: SERUM BY WEIGHT (T_w) FOR 14 AMMONIATED FIELD LATICES AND BROKEN LINE FOR AVERAGE OF 924 SAMPLES REPORTED IN PART I.

DISCUSSION

Viscosity: D.r.c.—In a previous communication[5] we fitted, to data for the viscosities of latex-serum mixtures, an equation of the form:

$$\log(\eta+c)=\log(\eta_o+c)+br \tag{7}$$

But when there are no observations at very low d.r.c., the value of c in Equation (7) cannot be satisfactorily evaluated, and it is sufficient, for empirical purposes in the region of 30 to 60 per cent d.r.c., to work with the linear equation:

$$\log\eta=a+br \tag{8}$$

as has been done above (Equations 4 and 5). Here a is an arbitrary constant greater than $\log\eta_o$.

In the previous paper, we noted that the viscosity of diluted latex agreed fairly well with Guth's theoretical equation (derived from an elaboration of Einstein's theory) up to 15 per cent d.r.c. Unfortunately when writing that paper, we overlooked that Guth's equation[6] had been later modified by Guth, Gold and Simha to:

$$\eta/\eta_0 = 1 + 2.5\phi + 14.1\phi^2 \qquad (9)$$

where η_0 is the viscosity of the suspension medium and ϕ is the volume concentration. This revised equation agrees fairly well with viscosity of diluted latex up to 30 per cent d.r.c.[7]

The data and formulas presented in this series of papers have been compared with available published data[8], as well as with Guth's equation. All show general agreement in principle, although they exhibit considerable variation in detail. Owing to differences in material and methods (types of viscometers; method of expressing concentration, *e.g.*, weight or volume, total solids or dry rubber; using water or serum as the diluent and as control for determination of "relative" viscosities; variations in soluble and insoluble serum solids, affected by the period of storage of the latex, etc.) a critical comparison is difficult, and presentation of a review would seem to serve little useful purpose.

Viscosity: Temperature.—Equation (2) implies that the viscosity of latex relative to viscosity of water is independent of temperature. Presumably this means that the viscosity-temperature curve of water shows viscosity proportional to that of the dispersion medium of latex; and Equation (2) is in accordance with Einstein's theory in so far that it indicates that the viscosity of a suspension relative to the viscosity of its suspension medium may be a function of concentration independent of temperature.

For critical work, attention should be paid to the solids content of serum, distinguishing between dissolved substances and suspended or colloidal particles. Since (by the Einstein-Guth theory) all solid substances in suspension are expected to affect viscosity independently of its specific character and of temperature (except in so far as temperature may affect the volume concentration), the cause of variations in slope of $\log\eta$: temperature curves of different latices should presumably be sought in the character and proportion of soluble substances in the serum. For solutions of nonelectrolytes, η/η_w decreases with temperature, whereas for solutions of electrolytes it increases[9]; therefore for an investigation of deviations of the curves for individual latices from Equation (2), which are usually in the direction of η/η_w decreasing with temperature, one might take as an initial hypothesis that the differences of slope may be correlated with the proportion of soluble nonelectrolytes in serum.

It follows further from Equation (2) that viscosity observations on latex or latex-water mixtures can be adjusted for temperature by the formula:

$$\eta_v = \eta_u \frac{\eta_v'}{\eta_u'}$$

where η_u is the viscosity of latex at temperature u, etc.;
η_u is the viscosity of water at temperature u, etc.;
u is the temperature of observation;
v is the temperature at which the estimation of viscosity is required.
η_u' and η_v' can be obtained from tables (*e.g.*, *Critical Tables*) or, if none such be available, can be calculated from Equation (3).

This merely confirms the basis of the correction put forward by Jordan, Brass and Roe[10]; but the formula above is both more precise and more general, and is applicable for any temperature range. Jordan, Brass and Roe noted that the temperature correction suggested by them was possibly an underestimate, but doubted the significance of a further digit estimated from their data. This paper indicates that their formula can be made more accurate as follows:

$$\eta_{25}=\eta_t\{1+0.023\ (t-25)\}$$

For adjustments around 15° C the coefficient is 0.026.

SUMMARY

The relation of viscosity of latex or latex-water mixtures to temperature and d.r.c. can be described, to a first approximation, by an equation of the form:

$$\log\eta=\log\eta_w+a+br$$

where η_w, the viscosity of water, indicates the change due to temperature; r=the ratio of rubber to serum (≒d.r.c/(100−d.r.c.)); and a and b are arbitrary constants.

Apparently the *relative* change of viscosity with temperature depends only on the suspension medium (serum), in accordance with the theory of viscosity of suspensions put forward by Einstein; and the viscosity of serum from 15 to 80° C is approximately proportional to that of water. A formula for $\log\eta_w$ as a cubic polynomial of temperature from 15 to 80° C has been evaluated (Equation 3); but for practical use, *e.g.*, in making temperature adjustments of observed viscosities, it is usually more convenient to obtain the values of η_w from a published table.

Values of a and b for a series of concentrate-water mixtures, and of ammoniated field latices, are given in Equations (4) and (5). Up to about 30 per cent d.r.c., the relative viscosity of latex seems to agree with the theoretical equation put forward by Guth for suspensions of spherical particles.

ACKNOWLEDGMENTS

I am indebted to Edgar Rhodes and K. C. Sekar for the use of unpublished data observed in this laboratory by Che Abdul Wahid bin Abdul Wahab; and to W. S. Davey for criticisms during the writing of this paper.

REFERENCES

[1] Rhodes, *J. Rubber Res. Inst. Malaya* **9**, 189 (1939); RUBBER CHEM. TECH. **12**, 665 (1939).

[2] The latices and latex-serum mixtures, for which data were reported in Part I, were clarified by passing through a 100-mesh sieve.

[3] There are two misprints in Table 1 of Communication No. 242 (*J. Rubber Res. Inst. Malaya* **9**, 189 (1939); RUBBER CHEM. TECH. **12**, 665 (1939):
Latex of Figure 6, 38.6% d.r.c., 55° C: for 3.1 read 2.8.
Latex of Figures 6, 59.4% d.r.c., 80° C: for 18.0 read 18.8.

[4] On Figure 7 and on Figure 8, m should be designated as the mean of log relative viscosity.

[5] Rhodes and Smith, *J. Rubber Res. Inst. Malaya* **9**, 171 (1939); RUBBER CHEM. TECH. **13**, 474 (1940).

[6] Guth and Gold, *Phys. Rev.* **53**, 322 (1938).

[7] In comparing the observations with Guth's equation on graphs representing log η *vs.* r, it should be noted that the curve of Guth has a point of inflection at $r_v=0.0888$, where $r_v=\phi/(1-\phi)$. Therefore an estimation of the slope of a curve such as (7) at zero concentration (as in Part I) is irrelevant for a critical comparison with Einstein's theory. A further point to note in comparing latex viscosities with the theory of Einstein or that of Guth is that ϕ represents the volume of total suspended substances, and if serum contains suspended or colloidal particles, it is not strictly the suspension medium appropriate for comparison with that theory.

[8] Blow, *Trans. Faraday Soc.* **25**, 458 (1929); Bary, *Rev. gén. caoutchouc* **11**, 3 (1934); RUBBER CHEM. TECH. **7**, 634 (1934); Bächle, *Kautschuk* **12**, 210 (1936) RUBBER CHEM. TECH. **10**, 675 (1937); Schmidt and Stamberger, *Rec. intern. rubber congr. Paris*, **1937**, 42; RUBBER CHEM. TECH. **11**, 479 (1938). Blow noted that latex-serum mixtures up to about 6 per cent d.r.c. agreed approximately with Einstein's theory. A further paper which has only recently come to the attention of the present author is that by Dogadkin and Kovarskaya (RUBBER CHEM. TECH. **11**, 630 (1938). Changes in viscosity are reported, both with temperature and with d.r.c., for dilutions of concentrated latex, Revertex, etc., are much lower than those reported above.

[9] Hatschek, "The Viscosity of Liquids", Bell Sons, Ltd., London.

[10] Jordan, Brass and Roe, *Ind. Eng. Chem. Anal. Ed.* **9**, 182 (1937); RUBBER CHEM. TECH. **10**, 615 (1937).

DISCOLORATION OF DRIED LATEX FILMS *

C. M. Blow

In the course of work on the application of latex to textiles, a staining effect was encountered which is the subject of this short note.

Briefly stated, an uncompounded concentrated latex was applied to a cotton fabric; some months after manufacture, pink-brown stains developed. The appearance of the stain suggested iron, and both the circumstances and further facts indicated that light was a likely contributory factor.

It was established that oxalic acid would not remove the stain, although this fact did not entirely rule out iron, since the rubber possibly prevented access of the oxalic acid. Furthermore, the stain was not removed by acetone, nor was it affected by a soap and soda scour, whereas if the fabric was treated with cobalt linoleate solution so as to oxidize the rubber, the stain was removed with the rubber in the course of subsequent scour. This suggested that the stain was associated with the rubber.

An investigation was therefore commenced on the effect of light on the color of dried films of latex in the absence, and in the presence, of iron. The results obtained appear of some interest, and have revealed a phenomenon not previously recorded as far as the author is aware.

To facilitate handling, pieces of filter paper (Whatman No. 1) were saturated in the latex or other test solution and dried off. The treated paper was exposed in a Fugitometer for 24, 48, and 72 hours.

The first observation was that a small percentage of iron (approximately 0.25 per cent Fe on the rubber), added to a centrifugally concentrated latex, gives a yellowish-brown film which, on exposure to sunlight or its equivalent, the carbon arc, develops many times in intensity to a dark brown. It may be noted that heat treatment at 70° C does not produce any such effect. The iron was added to the latex as a dilute solution of ferric chloride, which was precipitated by the ammonia present as colloidal ferric hydroxide.

A control test of the latex containing no added iron showed only slight discoloration on exposure, due, it is assumed, to the presence of traces of iron from the containers in which the latex is transported.

The following experiments were designed to find the responsible ingredients.

A filter paper, treated with ferric chloride and subsequently with ammonia to give a ferric hydroxide saturated paper, showed, as expected, no discoloration on exposure.

Portions of the paper, treated with latex containing ferric hydroxide, were boiled in water before exposure. In this case the development of the color was reduced, but by no means eliminated. Boiling in 5 per cent oxalic acid before exposure, however, had the effect of bleaching the paper and, at the same time, preventing almost entirely the development of staining on exposure.

Acetone-extraction of the paper was entirely without influence on the intensity of the discoloration which developed on exposure.

A sample of five-times-centrifuged latex which had been stored in an earthenware jar and appeared free of iron showed absolutely no yellowing on exposure.

* Reprinted from the *India-Rubber Journal*, Vol. 102, No. 31, page 610, January 31, 1942.

These experiments appear to establish that, to obtain the discoloration, iron, latex solids and light are essential.

It now remains to ascertain which particular ingredient of the latex solids is responsible. The experiments referred to above show that the acetone-soluble substances are not responsible, since acetone extraction is without effect.

The addition of iron to the five-times-centrifuged latex, the protein content of which is very small, produces a film which discolors markedly on exposure. This appears to eliminate the protein and water-soluble substances as the reacting ingredients. Filter paper treated with a solution of latex proteins, with or without the presence of ferric hydroxide, showed no discoloration; this is further evidence that the proteins are not responsible.

The indications are, therefore, that in the presence of light, ferric hydroxide forms with the rubber hydrocarbon, with an oxidation product of the rubber hydrocarbon, or with some substance (acetone- and water-insoluble) intimately associated with it, a pink-brown colored compound.

It is realized that the investigation is incomplete, but pressure of other work has not permitted further investigation. It was thought, however, that this brief note would record the observations made.

ACCELERATORS FOR LATEX

WATER-SOLUBLE VS. WATER-INSOLUBLE *

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It is of advantage to the latex technologist to be able to add compounding and vulcanizing ingredients as water solutions. With pigments, reinforcing agents, and fillers, there is little choice except to prepare aqueous dispersions, but in the field of accelerators, both water-soluble and water-insoluble materials are available. It would seem then that, given a suitable accelerator of each class, the water-soluble type would always be chosen for latex work.

There is one possible specific disadvantage in water-soluble accelerators, *viz.*, in compounds to be applied to porous surfaces. Such a disadvantage would seriously concern manufacturers of impregnated, coated, or pile fabrics, backed carpets, coated paper, and similar products involving the coating or impregnating of a porous surface with rubber from latex. These manufacturers consumed about thirty per cent of the 33,789 tons (dry rubber content) of latex used in the United States in 1940, and are thus major users of rubber latex accelerators.

TABLE I

BASE FORMULA

Rubber (from 60% centrifuged latex)	100.0
Sulfur	1.0
Zinc oxide	1.0
Casein	1.0
Fatty alcohol sulfate (Aquarex-D)	0.5
Accelerator	as shown

It has often been supposed that a latex compound to be coated onto a porous surface should not be accelerated with a water-soluble material. This supposition is based on the theory that the water-soluble accelerator would be absorbed, along with the latex serum, into the porous surface, and thus be largely lost. An examination of the literature revealed no published experimental work bearing on this theory. The experimental work reported in this paper was undertaken to supply quantitative data on this question.

The most obvious approach to this problem would be to mix a water-soluble accelerator into latex, pour a suitable quantity of the latex onto a porous surface, such as a fabric or porous porcelain plate, recover the serum which seeps into the absorbent material, and analyze it directly and quantitatively for accelerator. In practice, however, such a procedure presents many difficulties. To effect complete separation of the accelerator from the rubber, the porous surface selected must be impermeable to water-dispersed material but freely permeable to water-dissolved material. This is necessary because there are no accurate analytical methods for determining accelerators in the presence of rubber. These conditions of permeability also rule out the use of fabrics, since rubber in appreciable quantities either adheres to or is absorbed into them.

* Reprinted from *The Rubber Age* (New York), Vol. 50, No. 3, pages 195-198, December 1941. This paper was awarded Honorable Mention in the 1941 Papers Contest by the New York Rubber Group.

Unglazed porcelain plates were found to satisfy the conditions of permeability, and were selected for this work. However, when compounded latex was poured onto such porous plates and the top sealed to prevent evaporation, most of the serum was absorbed into the pores of the plate, and only a small quantity seeped through. Such a small quantity of serum made impossible accurate chemical analysis. In view of these facts, it was necessary to devise an indirect method of determining accelerator loss.

A practical indirect method consists of pouring the latex containing the water-soluble accelerator onto the porous surface in such quantity that the film dries completely by serum loss through the plate. Such a film is about 0.05-inch thick. A comparison between the physical properties of these films and films from the same compound made by casting on a glass plate, where drying is by evaporation alone, should reveal accelerator loss in a slower rate of cure for the porous plate films, since it is well known that reducing the amount of accelerator results in a slower rate of cure. Other physical properties, *e.g.*, modulus and tensile strength, may be affected, either by loss of accelerator or because of a change in the nature of the surface on which the film is cast. These two possibilities can be differentiated by running analogous experiments with water-insoluble accelerators to remove the possibility of accelerator loss.

Four widely used dithiocarbamate accelerators, two of which are water-soluble and two water-insoluble, were chosen for comparison. Dithiocarbamates were chosen because members of this class have exhibited wide general utility as accelerators for latex. The water-soluble accelerators—sodium dibutyldithiocarbamate (I) and hexamethyleneammonium hexamethylenedithiocarbamate (II)—were used as fifty and ten per cent solutions, respectively. The water-insoluble accelerators—zinc dibutyldithiocarbamate (III) and zinc diethyldithiocarbamate (IV)—were used as thirty-three per cent aqueous dispersions. The two salts of dibutyldithiocarbamic acid were chosen to obtain a comparison between a water-soluble and a water-insoluble salt of the same acid. The latex compound selected had the base formula shown in Table I.

The quantities of sulfur and zinc oxide in the base formula (Table I) are commonly considered adequate for good vulcanization. No antioxidant was used in the compound because it was desired to study the influence of the accelerator alone on the aging characteristics of the vulcanizates.

Glass-plate test films were made from the latex compounds according to the method of Wohler[1] as modified by Dales and Ayscue[2]. Porous-plate test films were made according to this same procedure, except that round, unglazed, porous, porcelain dinner plates, having an inside diameter of 6 inches, were used in place of glass plates. The inside bottom surfaces of these plates were ground so that level surfaces were formed when the plates were anchored by means of adhesive tape to a flat-topped bench. A round film 6 inches in diameter, and uniformly about 0.05-inch thick, was formed when 60 cc. of latex mix was poured into a plate and allowed to dry at room temperature. Loss by evaporation was prevented by sealing the tops of the plates with cellophane.

The series of compounds was prepared and films were made and tested from them three times. The same lot of 60 per cent centrifuged latex was used for all three runs. Checks between runs were invariably within 10 per cent of each other. All compounds in a series were made at the same time, and films from them were poured and tested at the same time. After each run, the porous plates were thoroughly cleaned, and their permeability checked. Testing was

done on a standard Scott testing machine, according to A.S.T.M. Specification D-412-40T, using Die B ($\frac{1}{4}$-inch). The temperature of the testing room was maintained at 82° ± 2° F.

TABLE II

WATER-SOLUBLE ACCELERATORS GLASS PLATE VERSUS POROUS PLATE FILMS

Air-oven cure (min./°F)	Stress at 600 per cent elongation *	Tensile strength at break	Elongation at break
COMPOUND 1 †—ACCELERATOR I—SODIUM DIBUTYLDITHIOCARBAMATE—0.5 PART			
Glass-Plate Films—‡ Selected Cure: 5 minutes at 200°F			
5/200	1075	5000	900
10/200	900	4800	900
20/200	1000	5000	920
30/200	925	5000	910
60/200	925	4825	935
Porous-Plate Films—Selected Cure: 5 minutes at 200°F			
5/200	875	4950	910
10/200	775	5175	930
20/200	775	5300	940
30/200	650	4025	880
60/200	600	4250	920
COMPOUND 2—ACCELERATOR II—HEXAMETHYLENEAMMONIUM HEXAMETHYLENE-DITHIOCARBAMATE—1.0 PART			
Glass-Plate Films—Selected Cure: 30 minutes at 200°F			
5/200	525	5150	940
10/200	1275	4075	810
20/200	1300	5100	840
30/200	1450	5525	890
60/200	1300	5275	850
Porous-Plate Films—Selected Cure: 30 minutes at 200°F			
5/200	500	4375	920
10/200	900	4800	900
20/200	1200	4975	870
30/200	1350	5200	875
60/200	1050	4350	830

* Tensile strengths and stress at intermediate elongations throughout this paper are given in English units (lbs. per sq. in.).

† Accelerator concentrations are given in parts on the dry rubber in the selected base formula.

‡ Selected cure is the cure at which the highest moduli are attained and is used to measure rate of cure.

RATE OF CURE

Since the indirect method of determining accelerator loss depends on the relation between rate of cure and accelerator content, the first comparison between films was made from this standpoint. Table II gives a comparison between glass-plate and porous-plate films made from compounds containing the water-soluble accelerators. This comparison shows that the same rate of cure, judged by moduli at 600 per cent elongation, is produced in both types of films, indicating no loss of accelerator. However, the moduli and tensile strengths of the porous-plate films are generally lower than those of the glass-plate films. That this is caused by the change in type of surface rather than loss of accelerator is shown in Table III. The data in Table III show a similar inferiority for porous-plate

films made from compounds containing the selected water-insoluble accelerators where accelerator loss is precluded by the nature of the porous plate.

The particular concentrations of accelerator, based on the dry rubber content of the compound, were chosen for the above comparison because such concentrations represent quantities generally used in latex compounding. It is possible, however, that the activity of these accelerators is so great that the loss of even

TABLE III

WATER-INSOLUBLE ACCELERATORS GLASS PLATE VERSUS POROUS PLATE FILMS

Air-oven cure (min./°F)	Stress at 600 per cent elongation	Tensile strength at break	Elongation at break
COMPOUND 3—ACCELERATOR III—ZINC DIBUTYLDITHIOCARBAMATE—1.0 PART			
Glass-Plate Films—Selected Cure: 30 minutes at 200°F			
5/200	425	2000	900
10/200	475	3725	990
20/200	675	5225	1000
30/200	825	5150	990
60/200	775	5350	1020
Porous-Plate Films—Selected Cure: 30 minutes at 200°F			
5/200	325	2750	960
10/200	475	4225	980
20/200	550	3775	960
30/200	775	4550	895
60/200	700	4125	900
COMPOUND 4—ACCELERATOR IV—ZINC DIETHYLDITHIOCARBAMATE—1.0 PART			
Glass-Plate Films—Selected Cure: 30 minutes at 200°F			
5/200	675	3600	980
10/200	875	5050	1000
20/200	1075	4800	900
30/200	1100	5200	930
60/200	1050	4650	910
Porous-Plate Films—Selected Cure: 30 minutes at 200°F			
5/200	625	3300	930
10/200	825	3800	910
20/200	875	4350	880
30/200	950	4775	880
60/200	875	4075	840

a considerable part of them, when the latex compounds were poured on porous plates, might not have been detected in stress-strain figures. This would be true if the rate of cure produced by the higher concentration of accelerator was no faster than that produced by some substantially lower concentration. For this reason, other compounds were made, using one-half as much accelerator as originally used, and films from them were compared.

The data obtained from this comparison are shown in Tables IV and V. It will be noticed that, as in the case where a higher concentration of accelerator was used, the water-soluble accelerators (Table IV), I and II, produce the same rate of cure in both glass-plate and porus-plate films and the tensile strengths and moduli are again lower for the porous plate films. Table V shows that this is again due to the change in surface on which the films were cast by showing a similar inferiority for the porous-plate films made from compounds containing the water-insoluble accelerators, III and IV.

That the reduced concentration of accelerator produces a slower rate of cure is shown in Table VI. In all cases, the rate of cure produced by the lower concentration of accelerators is considerably slower. Thus, it is practically certain that any appreciable loss of accelerator would have been revealed if there had been such a loss when a higher concentration of accelerator was used.

TABLE IV

WATER-SOLUBLE ACCELERATORS GLASS PLATE VERSUS POROUS PLATE FILMS

Air-oven cure (min./°F)	Stress at 600 per cent elongation	Tensile strength at break	Elongation at break
COMPOUND 5—ACCELERATOR I—SODIUM DIBUTYLDITHIOCARBAMATE—0.25 PART			
Glass-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	500	4550	1040
10/200	475	4275	1010
20/200	575	4600	990
30/200	700	5125	1000
60/200	750	5100	990
Porous-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	575	4250	960
10/200	625	4125	940
20/200	600	3900	890
30/200	650	3875	890
60/200	675	4175	895
COMPOUND 6—ACCELERATOR II—HEXAMETHYLENEAMMONIUM HEXAMETHYLENE-DITHIOCARBAMATE—0.5 PART			
Glass-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	775	4875	970
10/200	825	4400	920
20/200	1025	5125	900
30/200	1050	5325	900
60/200	1200	5075	860
Porous-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	825	5075	930
10/200	850	5275	930
20/200	875	5100	920
30/200	875	5050	910
60/200	900	4900	895

AGING

Quite often differences in vulcanizates are revealed more readily by other properties than by the stress-strain properties of freshly-cured stocks. This possibility may be investigated by measuring the resistance to aging of films from compounds containing water-soluble accelerators. If porous-plate films, which already have been shown to have the same rate of cure as glass-plate films, from the compounds containing the water-soluble accelerators are less resistant to aging than the glass-plate films, then an indication of accelerator loss from the porous-plate films is given, unless it can be shown that the poorer aging is due to the nature of the porous-plate films rather than loss of accelerator.

Table VII shows the results obtained when films having the selected cure from compounds containing accelerators I and III were aged in an air bomb 60 minutes at 80 pounds' air pressure and 260° F. Accelerators I and III were chosen for

this test because they are salts of the same dithiocarbamic acid. Selected cures were aged because they represent the best cured samples.

The data in Table VII reveal that porous-plate films from compound 1 containing accelerator I (water-soluble) aged poorer than glass-plate films from the

TABLE V

WATER-INSOLUBLE ACCELERATORS GLASS PLATE VERSUS POROUS PLATE FILMS

Air-oven cure (min./°F)	Stress at 600 per cent elongation	Tensile strength at break	Elongation at break
COMPOUND 7—ACCELERATOR III—ZINC DIBUTYLDITHIOCARBAMATE—0.5 PART			
Glass-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	600	4650	1040
10/200	625	4950	1000
20/200	750	5150	980
30/200	775	5150	970
60/200	800	5125	960
Porous-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	525	3875	940
10/200	550	4375	960
20/200	575	4600	960
30/200	575	3950	930
60/200	675	4775	950
COMPOUND 8—ACCELERATOR IV—ZINC DIETHYLDITHIOCARBAMATE—0.5 PART			
Glass-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	325	1350	900
10/200	450	3325	980
20/200	625	4650	965
30/200	750	4825	950
60/200	900	5175	960
Porous-Plate Films—Selected Cure: 60 minutes at 200°F			
5/200	275	2500	960
10/200	425	3200	920
20/200	700	3800	870
30/200	775	4325	875
60/200	800	4675	860

TABLE VI

COMPARISON OF RATES OF CURE

Compounds	Accelerator	Selected cure (min./°F)		Minutes low conc. is slower than high conc.
		High conc. accel.	Low conc. accel.	
1 and 5	I	5/200	60/200	55
2 and 6	II	30/200	60/200	30
3 and 7	III	30/200	60/200	30
4 and 8	IV	30/200	60/200	30

same compound. That this poorer aging was not caused by accelerator loss, however, is shown by the fact that the porous-plate films from compound 3 containing accelerator III (water-insoluble) also aged poorer than glass-plate films from the compound. Further, it is shown that the loss in resistance to aging of the porous-plate films, compared with glass-plate films, is almost identical for both the

water-soluble and water-insoluble accelerators, indicating more strongly that the poorer aging of the porous-plate films is due to the nature of the films and not to accelerator loss.

These tests of the aging characteristics of films confirm the conclusion reached in the study of rate of cure that there is no loss of properties attributable to loss of accelerator through water-solubility.

TABLE VII

TENSILE STRENGTH RETAINED AFTER AGING SELECTED CURES 60 MINUTES IN AIR BOMB

Compound No.	Cure	Accelerator	Type of film	Tensile strength original	Tensile strength after aging	Per cent tensile strength retained *	Per cent porous-plate films are poorer than glass-plate films
1	5/200	I	Glass plate	5000	2825	56.5	—
1	5/200	I	Porous plate	4950	1450	29.3	52.3
3	30/200	III	Glass plate	5150	1900	36.9	—
3	30/200	III	Porous plate	4775	875	19.2	52.0

* This figure obtained from the following relation:

$$\frac{\%\ \text{Tensile Retained by Porous-Plate Films}}{\%\ \text{Tensile Retained by Glass-Plate Films}} \times 100 = \%$$

CONCLUSIONS

The data presented in this paper support the following conclusions:

Little, if any, accelerator is lost when rubber latex compounds containing water-soluble accelerators are applied to porous surfaces.

The indirect method of analysis used is sensitive enough to detect any appreciable loss of accelerator, and would have detected any loss large enough to have practical importance.

The fact that films from a rubber latex compound, made by casting on a porous plate, have lower moduli and tensile strengths and are less resistant to aging than films made by casting on a glass plate, is apparently due to the physical nature of the porous plate.

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THE IMPREGNATION OF COTTON YARNS WITH LATEX *

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Ever since rubber has been appearing on the market, not only in the form of crepe or sheet, but also as latex with a rubber content of 40 per cent or more, numerous methods have been suggested for the direct impregnation of textile fibers with latex. The advantages connected with the substitution of latex for rubber solutions have already been reported[1].

Impregnation is here understood to be the penetration of rubber between individual fibers of yarn and not penetration into the fiber itself. Stevens and Stevens[2], in refuting British patent No. 178,811 of Hopkinson[3], have shown conclusively that penetration into the fiber itself is not possible, since the latex particles are larger than the pores of the fibers. In the case of ideal impregnation of yarn, therefore, each fiber would have a thin coating of rubber on its surface.

In the first section of the present article, various impregnation methods are mentioned. According to one process, good impregnation of yarn and cord can be obtained by using wetting agents like Igepon-T, and the aim of the present investigation was to obtain a closer knowledge of impregnation when using wetting agents. It is clear that in these impregnation tests, and also in impregnations on a commercial scale, determination of the amount of penetration is of special importance. This can be accomplished directly by microscopic examination of the cross-sections of the impregnated yarn. Before the actual impregnation tests could be started, it was therefore necessary first of all to develop a good method of preparing these cross-sections, since no satisfactory method is known to have been described in literature.

In addition to this visual determination of the degree of impregnation, other means were tried in evaluating the effect of the impregnation method employed. To this end the weight of rubber absorbed by cord was determined after each impregnation. As the results show, this method does not give a clear picture of the amount of impregnation obtained, since a considerable, though not constant, portion of the rubber is deposited on the outside of the yarn. One of the mechanical properties of cord which is favorably influenced by impregnation with rubber is fatigue resistance; consequently the treated cords were subjected to fatigue tests.

In this connection, it developed that, by impregnating in conjunction with a wetting agent according to the method indicated in the third section below, considerable improvement in fatigue resistance was obtained.

METHODS FOR IMPREGNATING YARNS WITH LATEX

When yarns and fabrics are impregnated with latex, it is found that, unlike solution impregnation, the rubber is not anchored to the yarn in a satisfactory manner, because the rubber from the latex does not sufficiently penetrate the interstices between the fibers. To achieve proper penetration in a simple manner is not easy, as is evident from the widely different methods already proposed[3]. Some typical methods are mentioned below.

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Preliminary Treatment of the Cotton

Schilthuis[4] ascribed the poor impregnation obtained with latex to the low capillarity of the cotton surface. He improved this capillarity by treating the cotton with an alkali and soap solution under pressure at 125° C. After this treatment the material was dipped into latex, and the surplus latex removed. The degree of penetration was calculated from the change in the specific gravity of the yarn, which was determined by means of a pycnometer. The improved penetration of the rubber was observed with the aid of a microscope, and was confirmed by fatigue tests.

Latex Treatment before Twisting

The principle of treating the fibers with latex before they are twisted into yarn was worked out by Lejeune and Bongrand[5] and by Pirelli[6], among others. According to this process, latex is sprayed on to the fleece of fibers before the fiber is spun on the spinning machine, and is then twisted into yarn in the usual way. By this means all the fibers in the yarn are coated with rubber.

Forcing Latex into the Yarn

In the Brandwood method[7] the yarn is wound on a hollow, perforated cylinder so that it does not overlap. The latex is forced through the walls of the cylinder into the yarn, and is then forced back in the opposite direction under a pressure of a few atmospheres at most. To assure thorough wetting, the fibers are first boiled in a solution of a sulfonated fatty alcohol. Duarry-Serra[8] even uses a pressure of several hundred atmospheres in forcing the latex into the fibers.

Spooling the Yarn in Latex

Ritzert[9] bends and stretches the yarn a few times while it is passing through latex. In this operation, the yarn is opened somewhat to permit penetration of the latex. A similar method is also used by Lejeune[10], who winds the yarn several times from one spool on to another after treatment with latex.

Adjustment of the pH

Bongrand[11] changes the pH of Revertex[12] from 11.4 to 5.2 by the addition of acetic acid and a stabilizer. When this mixture, which is more viscous than the original Revertex, is brought into contact with fibers having an alkaline reaction, the latex becomes less viscous and penetrates the fibers.

IMPREGNATION WITH WETTING AGENTS

Hauser and Hühnemörder[13] improved the penetration of latex rubber between the fibers of a yarn by employing wetting agents. They determined the reduction in surface tension of latex in the case of a large number of wetting agents, and determined their effect on impregnation with latex by microscopic observation of cross-sections prepared according to a method which they described[14]. According to Cotton[15], wetting agents are used in industry for impregnating jute; in this case the fabric is first soaked in a 0.5 per cent Igepon-T solution and, when partly dry, is dipped into the latex. Hauser and Hühnemörder also observed that when Igepon-T is used, it is advisable to treat the yarn with the wetting agent first and then with the latex, by which better results are obtained than by impregnation with a mixture of latex and wetting agent.

Since the literature references on impregnation with the aid of wetting agents give no further information about the method employed and the conditions which affect the degree of penetration, the investigation described below was instituted to obtain a more exact knowledge of this method of impregnation.

PREPARATION OF YARN FOR MICROSCOPIC EXAMINATION

It is practically impossible to cut thin sections for microscopic examination from soft vulcanized or unvulcanized rubber without special aids, and various methods have already been proposed to render the rubber suitable for this purpose. These methods can all be included under one of the following three processes:

1. Continued vulcanization of the rubber to a hardness approximately equal to that of ebonite by cold vulcanization[16] with sulfur chloride, or by hot vulcanization[17]. In the first instance, the degree of hardness of the rubber progressively decreases from the surface to the center and thus is not equally hard throughout; furthermore the sulfur chloride attacks the cellulose fibers so they cannot be cut. In the second case, the flow of the rubber may cause undesirable displacement of the rubber in the yarn[18].
2. Freezing the rubber and cutting by means of microtome[19]. The microtome required for this purpose is not available in every laboratory, and preparation of the sections is no simple matter by this method.
3. Embedding in a material[20] which rapidly becomes softer at a temperature of a few degrees above 0° C.

In many cases sections obtained by one of these methods are given a final treatment with strong sulfuric acid to burn the fibers away[17, 18, 21]. By this means, however, the finer details are often considerably distorted.

In the investigation of the impregnation of cord with latex, to be described later, it was found necessary, for microscopic control of the degree of penetration between the fibers of thread, to specify the following requirements: (1) rubber and fibers must remain intact and must not change their positions with relation to each other after the impregnation process; (2) fiber and rubber are to be plainly distinguishable from each other; (3) it should be possible to carry out the process in a fairly simple manner.

These requirements are satisfied by a method employing celluloid as the embedding material, which is described below and was adapted from the method which Kronacher and Lodemann[22] used for making samples for the microscopic study of wool fibers. Good results were obtained with this method in the laboratory for Technical Botany of the Technological Institute of Delft[23]. Kronacher and Lodemann describe the method as follows.

One end of unraveled wool fibers is adhered to a piece of paper by means of a drop of sealing wax. After the wax has hardened, the hairs are combed parallel to each other; then the free end is attached to the paper with wax. Next the paper is mounted on to a level board and held in place by thumb tacks to prevent it from curling during subsequent treatment. Over the prepared bundle of fibers is poured a layer (two millimeters thick) of a solution of 35 grams of celluloid in 170 grams of acetone to which four grams of Merck's Oil Black-O may be added if desired. Care should be taken that the acetone does not come in contact with the sealing wax at the ends of the fibers, since this would soften the wax and the fibers would not remain stretched. After about eight hours, the acetone has evaporated sufficiently to allow the celluloid to become hard enough for cutting. If kept longer than 24 hours, the celluloid becomes too hard, but

can be softened again by keeping the preparation for some time in a desiccator over acetone.

After drying, a strip of the paper to which the celluloid-coated fibers have been adhered is cut out, clamped onto a microtome or ordinary cutting cork, and then thin sections are cut by means of a microtome or an ordinary razor. According to Kronacher and Lodemann, it is possible in this way to make sections as thin as 10 microns from thick horse hairs (diameter about 50 microns). Microscopic examination of the internal structure of the transparent fibers can be further aided by using dark-colored celluloid for embedding.

After the procedure for coloring the preparation was modified, the Kronacher-Lodemann method proved to be very well suited for cutting thin sections of rubber-impregnated yarn. It is undesirable to examine microscopically rubber-treated yarn when it is embedded in a dark material, since the rubber with its low degree of transparency would be hard to distinguish in the dark preparation.

This objection can be met by the following procedure. The impregnated yarn is attached to a piece of paper with the aid of sealing wax or concentrated Venetian turpentine applied at the ends, and this paper is pinned onto a small board. A solution of 35 grams of celluloid in 170 grams of acetone, to which eight grams of tricresyl phosphate have been added, is poured over about two-thirds of the length of the yarn so that contact of liquid with the ends of the yarn is avoided. The board with the embedded material is then placed into a thermostatically controlled cabinet for some hours at room temperature, followed by a short period at 30 to 35° C to evaporate the acetone. When the celluloid has become hard enough, the cord is cut out in a strip about four millimeters wide, and thin sections are cut from this by a cutting cork and an ordinary razor. These sections are colored on an object class for two minutes with a saturated solution of Sudan-III in a mixture of three parts alcohol, one part water, and one part glycerol. The surplus color is washed away with a mixture of equal parts of water and glycerol. When the sections thus obtained are viewed under the microscope in water or in a water-glycerol mixture, the lemon-yellow rubber, pale-pink celluloid, and uncolored fibers can be plainly distinguished.

INFLUENCE OF WETTING AGENTS ON IMPREGNATION

The preparatory tests described below were made on bicycle tire cords, the composition of which follows:

Material	Unbleached cotton
Length of staple of fibers	22 millimeters
Number of twists in single yarn	16.7 per inch
Number of single strands of yarn	4
Number of twists in the twined cord	8.9 per inch
Contraction upon twining	4.9 per cent
Count of the single yarn	20 meters per gram
English metric number	12

A commercial, ammoniated 40 per cent latex was employed, which was diluted for these tests to a rubber content of 20 per cent. Of the numerous wetting agents mentioned in literature, Igepon-T[24], Sulfonated Lorol[25], and Igepon-AP[24] were selected.

A simple apparatus was constructed to permit impregnations to be carried out under conditions which would always be the same, and which could be varied as desired. This apparatus consists of a bath through which the cord is passed, and two small doctor-blades as well as a reel, driven by a small synchronous motor,

for winding up the impregnated cord. The bath and the blades are located on a table which can be moved parallel to the reel by means of a rope and tensioning weight. During impregnation, the table automatically moves past the reel, causing the cord to spiral about the reel. During the experiments, the cord was generally passed through the latex at the rate of 400 centimeters per minute so that it was immersed for two seconds. Where this rate of travel was changed, this is pointed out. After drying in air, the cord is removed, thoroughly dried above room temperature, and the amount of rubber taken up determined by weighing. The figures given are averages for five pieces of impregnated cord each about six meters long.

Certain factors, the influence of which on impregnation was not known, were investigated before proceeding, and it was found that: (1) the proportion of rubber taken up increases with the concentration of the latex, the fineness of the cord, and the temperature at which impregnation is carried out; (2) an ammonia concentration between 3 and 15 grams per liter of latex does not affect impregnation, and (3) air-dried cord containing 10 per cent moisture takes up about 20 per cent more rubber than absolutely dry cord.

From these facts, it therefore appears that in such tests temperature, concentration of the latex, and moisture content of the yarns must always be kept constant, while the NH_3 content of the latex may vary within the limits indicated.

Igepon-T

A very loosely twisted single yarn was passed through the latex bath to maintain contact with the latex for two seconds. After drying, the yarn was found to have taken up 80 per cent of its weight in rubber, but the microscope showed no rubber between the fibers. When, under the same conditions, the thread was first passed through a solution of 2 per cent Igepon-T in water, then dried, and drawn through the same latex bath, the thread took up 150 per cent of its weight of rubber, and the microscope showed that the rubber had penetrated between the fibers completely.

Next, the single yarn was replaced by the previously mentioned cord. When this was passed through the latex without a wetting agent, it took up 40 per cent of the fiber weight in rubber, all of which was on the outside, since the microscope nowhere disclosed rubber between the fibers.

When a solution of Igepon-T was added to the latex, as Table I shows, the proportion of rubber taken up by the cord slowly increased as the Igepon-T concentration was increased until, with a concentration of 10 grams of Igepon-T per 100 grams of rubber, the cord took up about 54 per cent of the fiber weight in rubber. Microscopic examination showed very little rubber penetrated between the fibers of the yarn. If, on the other hand, the cord was first passed through a solution of Igepon-T in water at the same rate, then dried in air, and subsequently passed through the latex, there was a considerable increase in the weight of the cord, even with low Igepon-T concentrations. After preliminary treatment with a 2 per cent Igepon-T solution, 80 per cent of the cord weight in rubber was taken up by the cord, and the microscope showed that, this time, the rubber had penetrated between the fibers, and had taken up about 50 per cent of the available space. These estimates are in the nature of the case only approximate.

Increased penetration of the rubber between the fibers was obtained by reducing the rate of passage to 36 centimeters per minute and, at the same time, prolonging the bath through the latex so that the fibers were in contact with the latex for 50 seconds. Under these conditions, and with the same preliminary treatment with a 2 per cent Igepon-T solution, the proportion of rubber taken up was about

68 per cent of the weight of the thread, and the microscope showed still further penetration between the fibers with about 80 to 100 per cent of the available space between the fibers found to be occupied by the rubber.

The difference between the two impregnation methods is that, in the one case, the wetting agent is concentrated on the surface of the fibers of the thread and, in the other, it is dissolved in the latex. The high concentration on the fiber surface greatly assists wetting, and at the same time the wetting agent presumably stabilizes the fibers and the latex with respect to one another. Thus, premature coagulation of the rubber particles on the outer surface of the thread is prevented, and all space between the fibers remains open to the penetrating latex. The rubber particles are, therefore, able to penetrate completely the interstices of the yarn, where the rubber dries after removal from the latex bath. Complete penetration also requires a definite period of time, as indicated by the improved impregnation of the thread after 50 seconds of contact with the latex, compared with a contact period of two seconds.

TABLE I

INCREASE IN WEIGHT OF CORD AFTER IMPREGNATION WITH WETTING AGENTS AT VARIOUS CONCENTRATIONS AND WITH A CONTACT PERIOD OF TWO SECONDS

Grams * wetting agent per 100 grams latex	Amount of rubber taken up, in percentage of the fiber weight					
	Wetting agent in latex			Treatment with wetting agent solution, then with latex		
	Igepon-T	Sulfonated Lorol	Igepon-AP	Igepon-T	Sulfonated Lorol	Igepon-AP
0	39	37	—	39	37	37
0.1	40	40	—	55	52	53
0.25	43	45	—	70	60	64
0.5	46	47	—	76	73	68
2.0	54	53	—	81	78	79

* Presumably the concentrations expressed in this column, "Grams wetting agent per 100 grams latex", refer only to "Wetting agent in latex." In connection with the last three columns of the table, "Treatment with wetting agent solution, then with latex", the concentrations in the first column undoubtedly represent the per cent concentration of wetting agent in aqueous solution.—EDITOR'S NOTE.

Although a reduction in the rate of travel through the latex and an increase in the contact period lead to better impregnation than with the original traveling speed and contact period, it was found that the cord took up a smaller proportion of rubber, *viz.*, 68 per cent against 80 per cent, based on the fiber weight. It might have been supposed that a more thorough impregnation would have been accompanied by a greater increase in weight of the cord.

However, a considerable portion of the rubber taken up is deposited on the outside of the cord, and the faster the cord is drawn through the latex bath, the heavier is this deposit and the greater the excess of latex. The latex dries on the outer surface and, although it adds to the weight of the fiber, it takes no part in actual impregnation. Here, then, the increase in weight is not a reliable measure of the degree of impregnation.

SULFONATED LOROL

The same tests as those carried out with Igepon-T were repeated with Sulfonated Lorol. In this case too, the cord was impregnated with a mixture of latex and wetting agent and with latex alone, after preliminary treatment with an aqueous solution of the wetting agent. As with Igepon-T, pretreatment with the wetting agent resulted in much better penetration between the fibers than when the wetting agent was added to the latex.

Reducing the rate at which the cord was drawn through the latex, and increasing the period of contact of the cord with the latex to 50 seconds, resulted in complete penetration so that, as the microscope showed, up to 100 per cent impregnation of the available space between the fibers was also obtainable by using Sulfonated Lorol.

Igepon-AP

Since Igepon-AP is not resistant to alkalies, no impregnation test was made with a mixture of this wetting agent and latex; the cord was impregnated only after preliminary treatment with the wetting agent. With the original rate of passage and contact period, 80 per cent of rubber was taken up by the thread,

Table II

Effect of the Method Adopted on the Degree of Impregnation of Bicycle Tire Cord with Wetting Agents

Method of impregnation	Contact period of cord with wetting agent or latex (seconds)	Dry material taken up percentage of fiber weight	Estimated penetration in percentage of the available space between the fibers
Single loosely twisted yarn:			
With latex alone	2	80	0
2 per cent Igepon-T solution, then with latex	2	150	100
Bicycle tire cord:			
With latex alone	2	40	0
2 per cent solution of Igepon-T in latex	2	54	5
First 2 per cent Igepon-T solution, then latex	2	80	50
First 2 per cent Igepon-T solution, then latex	50	68	80–100
2 per cent solution of Sulfonated Lorol in latex	2	53	5
First 2 per cent Sulfonated Lorol solution, then latex	2	78	50
First 2 per cent Sulfonated Lorol solution, then latex	50	60	80–100
First 2 per cent Igepon-AP solution, then latex	2	79	20
First 2 per cent Igepon-AP solution, then latex	50	62	60–80

but the microscope showed only about 20 per cent of the available space occupied by rubber. When the rate of passage through the latex was reduced and the contact period increased, the microscope showed 60 to 80 per cent of the available space taken up by rubber, although the weight of the thread was increased by only 62 per cent. Again the varying proportion of latex carried along was the reason for the discrepancy between the microscopic picture and the increase in weight.

The above results with the wetting agents mentioned are set forth in Table II.

Summarizing, we may conclude from these observations that:

1. Mixing the wetting agent with the latex causes only very slight penetration of rubber between the fibers of yarn.

2. Treatment of yarn with a wetting agent before impregnation with latex leads to better penetration of the rubber in the interstices than is possible by impregnation with latex alone or with a mixture of latex and wetting agent.

3. Prolonging the contact period of the thread with the wetting agent and with the latex causes the total proportion of rubber taken up to be lower than

when the thread travels more rapidly and the contact period is shorter, but the estimated penetration between the fibers is considerably greater.

4. By suitable selection of conditions and wetting agent, complete impregnation of a bicycle tire cord with latex is possible.

5. The increase in weight of thread after various treatments proves an unreliable standard for judging the degree of penetration.

FATIGUE TESTS WITH IMPREGNATED CORD

It has been found that a cord into which rubber has completely penetrated has a longer life, when repeatedly flexed, than a cord not so saturated with rubber. Therefore to determine whether the methods described, which, according to the microscopic picture gave varying degrees of impregnation, caused differences in the fatigue life of the cord, samples were subjected to fatigue tests. In these the cord was alternately quickly flexed and then stretched again, under not too great a tension, and this treatment was repeated until the cord broke. The duration

TABLE III

LIFE OF IMPREGNATED CORD

Method of impregnation	Life in minutes			Penetration of the available space between the fibers, in percentage (estimated) from microscopic picture see Table II)
	Minimum	Maximum	Mean	
Untreated cord	1	35	13	0
Two seconds with 20 per cent latex	8	28	16	0
Two seconds with mixture of latex with Igepon-T	10	38	16	5
Two seconds with 2 per cent Igepon-T solution, then two seconds 20 per cent latex	6	87	34	50
50 seconds 2 per cent Igepon-T solution, then 50 seconds 20 per cent latex	20	230	93	80–100
50 seconds 2 per cent Sulfonated Lorol, then 50 seconds 20 per cent latex	77	133	107	80–100
50 seconds 2 per cent Igepon-AP, then 50 seconds 20 per cent latex	4	100	49	60–80

from the beginning of the test up to rupture of the thread was taken as the measure of the resistance of the cord to fatigue.

In the literature, two types of apparatus for the fatigue testing of cord are mentioned; that of King and Truesdale[26] and that of Stavely and Shepard[27]. The first, also used by Schiltuis, is available at the Mechanical Technology Section of the Technical Institute[28]. The fatigue tests were carried out with this apparatus.

The King and Truesdale apparatus consists of two spindles along which a cord is led. One end of the cord is attached to a crank and rotated at a constant rate of 36 turns a minute. From the other end is suspended a weight which rises and falls when the crank is turned and keeps the cord taut.

The cord is led over two horizontal rolls, first passing over the upper roll, then between the rolls, and then under the lower roll; thus when the crank is turned the cord is sharply flexed locally and then stretched again. When the cord breaks, the weight falls on to a recording device, and the end of the test is accurately noted. The cord had a breaking strength of 2.7 kilograms and, in the fatigue test, was loaded with a weight of 450 grams. Table III shows the figures obtained with this arrangement, using 18 observations per cord.

Although these results have only a relative value, Table III indicates plainly that the methods followed, which revealed various degrees of impregnation under the microscope, also had a considerable effect on the fatigue resistance of impregnated cord. Taking into consideration that microscopic observations are only estimates, and that the fatigue results show deviations, it may be concluded that both these methods indicate that the impregnation process in which the cord is previously treated with a wetting agent is preferable. The action of the wetting agent here consists, not only in lowering the surface tension of the latex, but also in stabilizing the latex and the fibers with respect to each other, thus preventing coagulation on the outside of the cord.

SUMMARY

1. Thin sections of yarn impregnated with rubber can be made in a simple manner according to the modified Kronacher-Lodemann method here described; and fibers, rubber, and embedding material can be clearly distinguished.

2. Impregnation of a cord with latex in which a wetting agent is dissolved results in a far lower degree of penetration by rubber than impregnation with latex following treatment of cord with a solution of the wetting agent.

3. When the proper conditions and wetting agent are selected, bicycle tire cord previously treated with a wetting agent can be completely impregnated with latex.

4. There is a definite relation between the microscopic picture indicating the degree of penetration of rubber between fibers and the results of fatigue tests.

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NOTE ON THE PRODUCT OF A REACTION BETWEEN AQUA REGIA AND LATEX *

V. H. WENTWORTH

INTRODUCTION

Arising from experiments to repeat on fresh latex the halogenation experiments made by Baker[1] on ammoniated latex, the sodium chlorate and hydrochloric acid reagents were replaced by aqua regia. After numerous unsuccessful trials with different stabilizers and combinations of mixed acids, a method was evolved which produces a product in the form of a fine free-flowing powder. Sibley[2] stated in a recent lecture that a wide variety of products could be obtained from rubber by reaction with increasing proportions of aqua regia, and this note gives the details of a method of producing an interesting product by the action of aqua regia on rubber in the form of fresh latex.

METHOD

In a water bath arranged to admit a flow of cold water, set up a six-litre bolt-head flask fitted with a mechanical stirrer and a dropping funnel. Place 100 cc. of fresh latex (35-40 per cent dry rubber content) in the flask and stir in 24 grams of Lissapol A paste mixed with 200 cc. of water, followed by 600 cc. of concentrated hydrochloric acid. The temperature of the water surrounding the flask should be about 50° C initially, and when the contents reach this temperature, 150 cc. of concentrated nitric acid are run rapidly from the dropping funnel into the latex mixture with constant stirring. The reaction gradually gathers momentum, and the water in the bath heats up rapidly if not changed but, by admitting a steady stream of cold water to the bath, the reaction can be controlled and the temperature of the reactants kept down to about 80° C. Copious fumes of nitrogen peroxide are at first evolved, but when these have subsided, the water is run out of the bath and the reaction mixture is allowed to stand overnight.

The product is a fine yellowish-brown powder, which settles readily and is easily washed by decantation, finally filtered on a Buchner funnel and dried in a vacuum desiccator.

OBSERVATIONS MADE DURING DEVELOPMENT OF THE METHOD

If the above procedure is used, except that the temperature of the reacting mixture is kept below 10° C by the use of ice, the product is not homogeneous—part is rubbery and the remainder has the texture of brown factice. If the initial temperature is not more than 25° C, the reaction temperature does not rise above 30° C, and a brown coagulum forms. The addition of nitric acid before the hydrochloric acid is not so effective as the order recommended.

It was thought that the reaction might be more readily controlled if the latex was at a sufficiently high temperature to cause instantaneous reaction, and experiments were made accordingly.

Latex in the presence of Lissapol A and hydrochloric acid coagulated when the temperature approached 100° C; when the acid was omitted, a thick paste formed

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at that temperature. Latex and stabilizer without acid remained liquid at 80° C, but hard lumps were formed when the previously mixed hydrochloric and nitric acids were added. At 70° C, in the presence of hydrochloric acid and stabilizer, the latex remained fluid but, on addition of nitric acid, coagulation occurred. Commencing with the latex and acid mixture at 60° C, all the nitric acid was added before flocculation occurred, but lumps were formed when the vigorous reaction set in. However, it was found that, on a Buchner funnel, these lumps readily broke down to a fine powder. An initial temperature of 50° C was found to be best. Doubling the amount of stabilizer did not appreciably increase the stability of the mixture.

Other variations included running the cold stabilized latex and hydrochloric acid mixture into nitric acid at 80° C. This was fairly successful; the product looked more granular, but was easily pressed to a fine powder. Interchanging the acids and running a latex-nitric acid mixture into hot hydrochloric acid was unsuccessful, a mixture of brown and yellow granules being produced. The stabilizer sold as Vulcastab was found to be suitable but Vultamol, casein and saponine were not.

THE REACTION

Goldschmidt's equations for the reaction between nitric and hydrochloric acids in the presence of water are given below, but these do not fully represent the more complex reactions which occur[3].

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$$
$$NOCl + H_2O = HNO_2 + HCl$$

The reagents present provide possibilities for numerous reactions with rubber; Baker[1] has produced products with nascent chlorine under similar conditions; nitrosyl chloride will also attack the double bonds of the rubber molecule, and the acids are possible additive groups. In addition, oxides of nitrogen and products of side reactions not represented by the above general equations are likely to complicate the reaction still further.

PROPERTIES OF THE PRODUCT

The product is a yellowish-brown free-flowing powder, having more than double the weight of the original rubber in the latex. Ultimate analyses have not been made, but chlorine was estimated in the Parr Bomb and nitrogen by Kjeldahl; typical results are N 5.3 per cent, Cl 26.1 per cent. It has not been ascertained whether the stabilizer contributes to the yield, but if it does not, the oxygen content of the product should be of the order of 20 per cent.

The powder is insoluble in water and sodium carbonate solution, but is soluble in caustic soda solution, changing to a dark brown on contact with the alkali. It is insoluble in dilute sulfuric acid, but dissolves in the cold concentrated acid, without decomposition. In aqueous ammonia it is only partially soluble and, when filtered, the residue on the filter paper dissolves in acetone but gives a much darker solution than the original powder. It does not decolorize bromine in carbon tetrachloride solution.

On warming to 80° C, the product softens and can be pulled out into brittle threads, but at 130° C thermal decomposition sets in, with rapid generation of heat and carbonization of the mass.

The following is a table of solubility in organic solvents:

Solvent	Solubility
1. Acetone	Soluble
2. Ethyl acetate	Soluble
3. Ethyl lactate	Soluble
4. Butyl phthalate	Soluble
5. Ethyleneglycol monoethylether	Soluble
6. Triacetin	Soluble
7. Cyclohexanone	Soluble
8. Amyl acetate	Small insoluble portion
9. Isobutyl acetate	Small insoluble portion
10. *n*-Butyl acetate	Small insoluble portion
11. Tricresyl phosphate	Small insoluble portion
12. Ethyl alcohol	Partially or slightly soluble
13. Cyclohexanol	Partially or slightly soluble
14. Amyl acetate	Partially or slightly soluble
15. Chloroform	Partially or slightly soluble
16. Ether	Insoluble
17. Petroleum ether	Insoluble
18. Benzene	Insoluble
19. Toluene	Insoluble
20. Xylene	Insoluble
21. Cyclohexane	Insoluble
22. Decalin	Insoluble
23. Tetralin	Insoluble
24. Carbon tetrachloride	Insoluble
25. Trichloroethylene	Insoluble
26. Tetrachloroethane	Insoluble
27. Monochlorobenzene	Insoluble
28. Carbon disulfide	Insoluble

After storage for two years, a slight acrid odor and a darkening in color is noticeable, but the general properties of the powder appear to be unchanged. Numerous possible technical applications appear to be worthy of investigation.

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THE ABSORPTION OF WATER BY RUBBER

I. METHODS OF EVALUATION *

V. H. WENTWORTH

Numerous procedures have been suggested for estimating the water-absorption capacity of crude rubber. These are based mainly on the determination of the increase in weight of samples, either after suspension in air of known humidity or after immersion in water at standard temperatures for fixed periods of time. The tendency has been for workers in Europe to adopt the former method, whereas the latter method is favored in America.

In general, simplicity of technique is the attribute of water-vapor tests, although it is probable that absorption of water solely in the form of vapor does not present a serious technical problem. Testing by both methods requires more elaborate apparatus for the preparation of test-pieces than is likely to be freely available in rubber-producing countries, although a smooth roll creping machine, if in good condition, might be used without a water spray to prepare a thin sheet for testing in water vapor. It is believed that a sufficiently good correlation exists between tests on the crude and manufactured product to enable a safe standard to be set for the crude material but, as in all such problems, service trials are the true criteria.

It is not the purpose of this paper to attempt to select one method of testing to the exclusion of another but, rather, to set out practical details for carrying out the tests and to specify the methods used in the Rubber Research Institute.

SUSPENSION-IN-VAPOR METHODS

Cooper and Daynes[1] examined two methods previously used by Lowry and Kohman, involving suspension of the sample in water vapor, and concluded that the direct measurement of the increase in weight of a rubber sample suspended in vapor is the most convenient method for repetition work, although they considered that a method in which unabsorbed water vapor is estimated by vapor pressure measurements is more accurate. Testing in vapor was also described by Skinner and Drakeley[2], and theoretical aspects were discussed by Daynes[3]; Okita[4] preferred to test in vapor rather than liquid because he considered the method was both more convenient and less liable to errors from oxidation.

The amount of water vapor absorbed within a given time depends on the surface exposed, and Skinner and Drakeley[2] concluded that ". . . . comparable results are only obtained in a reasonable time by using shredded samples of rubber." Using the method of shredding described by these authors (which is to pass the sample of rubber through a tightly closed mill with one roll stationary), the writer was unable to confirm their conclusion and found that, with the equipment at his disposal, a thin sheet was preferable to shreds. Further, it is more difficult to ensure the same degree of subdivision between shredded samples, whereas a sheet can be prepared within specified limits of thickness or weight per unit area.

* Reprinted from *The Journal of the Rubber Research Institute of Malaya*, Vol. 11, Communication No. 257, pages 59-78, October 1941.

Table I gives the absorption results obtained from six test-pieces prepared either in sheet or in shredded form from the same rubber sample after remaining in the same atmosphere of 84 per cent humidity at 90° F for eight days. The shredding was carried out on a 12-inch mill of roll diameter six inches, using a tightly closed nip. The front roll was not driven and the back roll revolved at 18½ r.p.m.

The results in Table I show that shredding as described gives less absorption than sheeting after eight days' exposure, although attempts were made to obtain the maximum surface by shredding as finely as possible.

A method of testing in water vapor has been used by the London Advisory Committee for Rubber Research (L.A.C.) for a considerable time, but only brief details have been published[5]. The Rubber Research Institute of Malaya (R.R.I.M.) has adopted the method, with slight modifications. In dealing with crude rubber, the method seems as satisfactory as any of the published methods, and the details of the test, as used in the R.R.I.M., are as follows.

TABLE I

ABSORPTION OF WATER-VAPOR BY SHEETED AND SHREDDED RUBBER

Form of rubber	Absorption (per cent)						Mean
Sheeted	0.495	0.486	0.477	0.472	0.467	0.463	0.477
Shredded	0.477	0.446	0.442	0.432	0.429	0.418	0.441

THE L.A.C.-R.R.I.M. VAPOR TEST FOR WATER ABSORPTION

1. Pass the sample of crude rubber twice through a cold mill, having tightly closed rolls, to produce a uniform thin sheet.

2. Using a Schopper circular knife (diam. 4.46 cm.), cut from the sheet the desired number of test-pieces. Four test-pieces per sample are usually taken.

3. Place in a closed container over a saturated solution of potassium chloride in a constant temperature room at 90° F for eight days. The relative humidity is approximately 84 per cent[6].

(The containers in use are specimen jars ten inches high and seven inches in diameter, in which three wooden uprights held eight sliding frames with threads stretched across, each frame carrying four discs of rubber.)

4. After eight days, remove the discs individually and weigh immediately.

5. Place in an oven maintained at about 90° C, and dry to minimum weight (about four hours).

6. Calculate the result as follows:

$$\text{Absorption} = \frac{\text{Wt. of wet disc} - \text{Wt. of dry disc}}{\text{Wt. of dry disc}} \times 100\%$$

The British Standards Institution has now published its "Methods of Testing Latex, Raw Rubber and Unvulcanized Compounded Rubber" (No. 902—1940), and the method of evaluating the "equilibrium water absorption" is very similar to the method described above. The differences are the use of one test-piece of about four times the area instead of four separate test-pieces, the specification of a test-piece thickness of one gram per 16 sq. cm. and the expression of the result as a percentage by volume instead of by weight (the above calculation can be corrected by multiplying by the density of the rubber).

The British Standards Institution method specifies that the test-sheet shall weigh approximately one gram per 16 sq. cm., and experiments were made to examine the effect of varying the thickness, since the mill at our disposal will not produce a sheet meeting this requirement except by inserting small pieces of rubber from which only one disc can be cut. Twenty-four discs were prepared from the same sample of rubber, increasing thicknesses being obtained by opening the "nip" of the mill. The discs were kept under the specified conditions for eight days, and were then weighed. As a matter of interest, drying was carried

TABLE II

INFLUENCE OF THICKNESS ON THE ABSORPTION OF WATER-VAPOR BY SHEETED RUBBER

No.	Weight per 16 sq. cm. gm.	Water-absorption from vapor (percentage) Dried 4 hours @ 70° C	Dried further 4 hours @ 90° C
1	0.45	0.45	0.54
2	0.55	0.54	0.65
3	0.57	0.51	0.69
4	0.68	0.54	0.70
5	0.72	0.53	0.81 *
6	0.72	0.50	0.58
7	0.95	0.59	0.63
8	1.13	0.53	0.60
9	1.21	0.58	0.61
10	1.21	0.58	0.63
11	1.23	0.56	0.64
12	1.25	0.54	0.59
Average		0.54	0.62
13	1.52	0.61	0.74
14	1.56	0.65	0.66
15	1.67	0.64	0.70
16	1.79	0.62	0.77
17	1.83	0.62	0.75
18	1.84	0.59	0.71
19	2.54	0.64	0.68
20	2.54	0.63	0.68
21	2.58	0.63	0.65
22	2.58	0.63	0.68
23	2.84	0.62	0.65
24	2.87	0.63	0.67
Average		0.63	0.69

* Not included in average.

out in two stages—for four hours at 70° C, followed by a further four hours at 90° C, and the discs were reweighed after each period, with the results given in Table II.

From these results it is seen that the thicker discs give higher absorption results than the thinner ones, and there is, therefore, no fear of underestimation when using apparatus which will not produce a sheet of the requisite thinness. It is possible that the reason for this is to be found in the greater masticating effect which occurs when preparing the thinner sheet and which is examined later in this paper.

Drying should be at 90° C and not 70° C, despite the fact that ovens maintained at the latter temperature are more common in rubber testing laboratories.

WATER-IMMERSION METHODS

Messenger and Scott[7] tested sole crepe by immersion in water, but the laminated nature of the material led to results not entirely due to the characteristics of the rubber. Daynes[3] rejected the liquid-immersion test because it required too long to reach a stage approaching saturation but, judging by its wide use, it is evident that the test is considered suitable for comparative purposes.

Boggs and Blake[8] proposed a method of testing which has received fairly wide adoption in its general form although the details have been amplified and slightly modified by Noble[9] and others[10] In broad outline, the Boggs and Blake test consists of moulding the rubber sample by heat and pressure to uniform dimensions, weighing the specimen, immersing in water at 70° C for 20 hours, drying the surface and reweighing. The increase in weight is expressed as milligrams of water absorbed per square inch of surface, a method of expression which is to be preferred to that of percentage absorption by weight for specimens of appreciable thickness because, as was demonstrated by Rowell[11], using Tufnol sheets, misleading conclusions can be drawn by reporting the results in this manner.

Van Dalfsen[12] has suggested the use of an immersion test differing widely from the earlier methods, but it is considered that there is no reason to justify a wide deviation from the outline of the Boggs and Blake procedure for the general classification of crude rubber, even if the facilities available may make it necessary to modify details. It is probable, however, that consumers, in particular, will use additional tests more closely resembling the service conditions their products have to meet. With this in mind, tests are also made at the R.R.I.M. by immersing for 14 days at 90° F (a tropical atmospheric temperature) in addition to 20 hours at 70° C.

The influence of different factors on the resistance of crude rubber to the absorption of water has been discussed by several authors. Evidence that oxidation increases the water-absorption capacity of rubber was put forward by Okita[4], Blake and Morss[13], and Robertson[14]. Boggs and Blake[8] considered that deproteinized rubber resisted oxidation as satisfactorily as normal rubber, but they observed considerable degradation of the rubber when the period of immersion was increased. Contradictory evidence has been reported by Soule[18] who exposed ribbed smoked sheet to extremely drastic conditions without deterioration. He suggested that the preliminary heating of the rubber involved in the Boggs and Blake method of preparing the samples for testing might have reduced its resistance. The work of Kemp[15], however, did not support this view; referring to plantation smoked sheet he stated that "if the sheets are heated in the press at 142° C for 1.5 hours, the rubber absorbs less water and becomes electrically more stable." This he attributed to heat hardening of the proteins; he found also that mastication was beneficial in improving the resistance to water absorption. It was evident, therefore, that the preliminary treatment necessary for the preparation of the sample should be carefully controlled if its subsequent behavior on immersion in water is affected.

To apply the Boggs and Blake method of testing to rubber in any form, while utilizing available apparatus, a technique has been developed which is described in this paper together with an account of the effects of the various factors in the procedure on the results obtained.

PREPARATION OF TEST-PIECES

In general, raw rubber to be tested for water absorption is in the form of thin crepe, which can be piled up to any desired thickness without preliminary treatment, but if smoked sheet or sole crepe has to be tested, the preparation of test-pieces of a standard thickness usually involves mastication of the rubber, which is undesirable. To avoid this difficulty, a method of testing applicable to raw rubber in any form was devised, with as little variation as possible from the method of Boggs and Blake.

In the Boggs and Blake procedure[10], the requisite number of crepe layers are placed between aluminum sheets in a frame, 0.08 inch thick, and are held in a platten press at 215° F for 30 minutes. The rubber is allowed to cool in the mould and, after removal, the sheet assumes a thickness of about 2.25 mm. (0.089 inch), from which test-pieces of size 4×1 inches are cut. Preliminary trials were carried out on the basis of these instructions, and steel moulds, without spewways, having an inserted aluminum base plate and an aluminum top plate were obtained, the size of the mould being intended to produce three test-pieces.

The press available for this work was a 12×16 inch steam-heated platen press, operated by a hand screw. For practical reasons it was found convenient to use it at 259° F (20 lbs. per sq. in. steam) instead of 215° F (1 lb. per sq. in steam), but the influence of temperature was one of the factors investigated before adopting the higher temperature.

Various types of rubber were pressed, but the mouldings were disappointing. The best results were obtained from blanks which almost filled the cavity and flowed very little. When pressing smoked sheet and sole crepe, the thickness could not be adjusted, and it was often necessary for a weighed blank to flow considerably, as a result of which moulding proved to be unsatisfactory. Spew-holes of various sizes were cut in the moulds, and these effected some improvement, but when a satisfactory moulding was apparently obtained, pronounced shrinkage occurred along the flow lines some time after removal of the sample from the mould. Twenty-four hours later only one test-piece of correct size could be cut from a moulding intended for three. A temporary improvement resulted from keeping the rubber in the mould for 24 hours, although it only postponed the distortion, which occurred after the test-piece had been cut to the correct size and immersed in water.

A reduction of plasticity and "nerve" by mastication was another expedient which assisted moulding, but the effect was only temporary, and the sheet subsequently developed a very uneven surface and was distorted. The use of any form of mould lubricant was considered to be undesirable.

It was found that much better test-pieces could be obtained by pressing the rubber between aluminum plates, without the restriction of a mould, and this proved to be the best method for rubber in any form, but the thicknesses of the resultant sheets differed. Allowances had to be made for these differences in the calculation of results. Although this method of pressing is well suited to a screw-type press distance, pieces may be required when using a press having a continuous hydraulic pressure.

The sheet was required to be of sufficient size for the cutting of six test-pieces each measuring 4×1 inches. Having adopted the above method of pressing, twenty-four aluminum plates, $11 \times 9\frac{1}{2} \times 0.125$ inches, were obtained to allow for the preparation of one dozen sheets per day. Smoked sheet, sole crepe, and thin pale crepe were cut to a size of $10 \times 4\frac{1}{2}$ inches, plied up when necessary, and placed between pairs of plates together with an embossed aluminum identification

tag. Each sample was pressed separately for 30 minutes at 259° F, and the press was retightened after 15 minutes. On removal from the press, the aluminum sheets were not separated, but were cooled under the tap, and placed under light pressure overnight in a small screw press of the office type. Test-pieces were then conveniently prepared from the smooth pressed sheets by placing them on parchment paper and cutting to a size of 4×1 inches on a photographic trimming board.

FACTORS INVOLVED IN TESTING BY THE IMMERSION METHOD

(a) Effect of the Temperature of Pressing on Water Absorption

In published descriptions of the immersion test, a temperature of 215° F (1 lb. per sq. in. steam pressure) has been prescribed for the press, but this was inconvenient with the apparatus at our disposal, and it was desired to use a steam pressure of 20 lbs. per sq. inch, if the results were not impaired. To examine the effect of press temperature, test-pieces were prepared by pressing at atmospheric temperature (85° F), at 259° F (20 lbs. per sq. inch) and at 307° F (60 lbs. per sq. inch). Neither ribbed sheet nor crepe was suitable for this particular test, since cold pressing was not capable of producing a smooth sheet, and a special batch of rubber was prepared for the purpose. The coagulum was

Table III

Effect of Press Temperature on Water Absorption

Temperature of pressing	Mean absorption (mg. per sq. in.) 20 hours at 70° C	14 days at 90° F
Approximately 85° F (atmospheric temperature)	25.7	39.4
259° F (20 lbs. per sq. in. steam)	25.6	37.6
307° F (60 lbs. per sq. in. steam)	27.0	39.8

quite normal but, during the machining, the final marking rolls of the sheeting battery were not used. The smooth sheet, free from ribbing, was dried in a smoke-house.

Samples were tested by immersion in water at 70° C for 20 hours at 90° F for 14 days, with the results given in Table III.

For practical purposes it appears that the results are not materially affected by the temperature of pressing used in the preparation of the test-pieces, under either of the conditions of immersion; a temperature of 259° F may be used instead of 215° F without prejudice to the results.

(b) Effect of Mastication on Water Absorption

As reported under "Preparation of Test-Pieces," mastication before moulding proved useful as an adjunct to moulding, but the test-pieces were subject to delayed distortion. The treatment found to be suitable for general use, with the minimum amount of working, was to pass the rubber 30 times through a nip of 0.020 inch in a 12×6 inch mill, having a differential of 1.4, and its rolls at 50° C. After pressing, the mould was cooled in water, but was left unopened for 24 hours until just before cutting the test-pieces from the moulded sheet.

In Kemp's method of testing[15], mastication for ten minutes and pressing between cellophane sheets was prescribed, but the author stated that mastication gave a beneficial effect. The data in Table IV verify this statement.

It was considered undesirable to submit samples to any treatment which reduces their water-absorption capacity, and it is useful to provide a safety margin by ensuring that test figures represent maxima. In addition, mastication conditions are difficult to define, and the necessary equipment is not usually available to rubber producers.

In examining the effect of mastication on water absorption, pressing between aluminum sheets was used without moulds, and the first tests were carried out on air-dried sheet having a normal nitrogen content of 0.32 per cent.

Sufficient rubber to provide twenty-four test-pieces was divided into two parts. One part was masticated as previously described; the other did not receive any pretreatment. After pressing at 259° F, twelve test-pieces were cut from both the milled and unmilled rubber, and six tests of each rubber were made under two different conditions of immersion. The results are given in Table IV.

TABLE IV

EFFECT OF MASTICATION ON WATER ABSORPTION

Conditions of immersion	Mean absorption (mg. per sq. in.)	
	Unmasticated rubber	Masticated rubber
20 hours at 70° C.....	24.3	16.1
14 days at 90° F.....	30.3	17.0

TABLE V

EFFECT OF MASTICATION ON THE WATER ABSORPTION OF CREPE OF MEDIUM AND LOW NITROGEN CONTENT

Conditions of immersion	Sole crepe (Nitrogen 0.26 per cent)		Low-nitrogen crepe (Nitrogen 0.06 per cent)	
	Mean absorption (mg. per sq. in.)		Mean absorption (mg. per sq. in.)	
	Unmasticated	Masticated	Unmasticated	Masticated
20 hours at 70° C.....	16.2	14.1	5.9	5.4
14 days at 90° F.....	28.1	22.7	8.8	8.6

The benefit of mastication is plainly evident, for it reduced the water absorption by 36 and 44 per cent, respectively, in the short and long period tests. This benefit will accrue in the course of manufacture with the rubber, and will serve as a margin of safety over test figures obtained on the crude rubber if mastication is avoided during testing.

In general, rubber to be tested for water absorption is in the form of crepe which has been subjected to a limited amount of mechanical working during manufacture. It was of interest, therefore, to examine the effect of mastication on sole crepe, and also on a crepe of low nitrogen content. The latter rubber was prepared from latex, which was treated with caustic soda, subsequently creamed, coagulated, and the coagulum creped.

Table V gives the mean absorption from groups of three test-pieces.

Mastication of sole crepe reduced the results by 13 and 19 per cent, respectively, in the short and long-period tests. The effect on crepe of low nitrogen content was small.

IMMERSION OF TEST-PIECES

(a) Method

The following practical details have proved satisfactory. Each test-piece is immersed in distilled water in a $6\times1\frac{1}{2}$ inch test-tube, covered by a watch glass, and retained below the surface of the water by means of a sinker made by fusing a hook to the side of a glass rod. The test-piece is pierced by the hook near one end. This causes the rubber to float vertically and completely immersed, as shown in the figure. By this means, any tendency of the rubber to curl up on itself is eliminated. The tubes are conveniently contained in racks to hold six. By the use of individual containers, labelling is facilitated, and estimations of extracted material can be carried out by evaporation of the water.

At the end of the test, the samples are removed from the water one by one, wiped dry with a lintless cloth, and weighed within two minutes. They are then left in an oven at 90° C overnight, and reweighed when dry. By using this latter

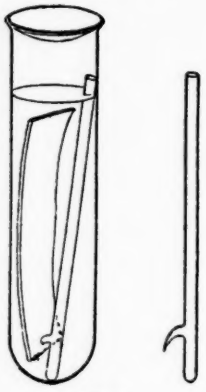

Fig. 1.

weight instead of the weight of the original test-piece, losses due to leaching out of water-soluble substances are minimized, and the moisture content of the sample before immersion is included.

(b) Effect of the Volume of Water in Which a Test-Piece Is Immersed

If the surface of a rubber test-piece acts as a semipermeable membrane, and absorption is in part due to different osmotic conditions on either side of the membrane, it is possible that variations might result from differences in the concentration of soluble material leached from the rubber into large or small volumes of water. It is known also that the absorption of water from a salt solution is less than that from distilled water[7, 16].

To examine the possible effects of different volumes of water, a thin sheet of sole crepe was pressed, and from it eighteen test-pieces were cut. Groups of three were tested in different volumes of water, each test-piece having a separate container. The results are given in Table VI.

The figures in Table VI indicate that the volume of water used in the test need not be closely specified. A convenient quantity is 120 cc., contained in a $6\times1\frac{1}{2}$ inch test tube.

TABLE VI

THE EFFECT OF THE VOLUME OF WATER ON ABSORPTION

Volume of water in which each test-piece was immersed (cc.)	Immersed for 20 hours at 70° C		Immersed for 14 days at 90° F	
	Mean gauge of three test-pieces (inch)	Mean absorption (mg. per sq. in.)	Mean gauge of three test-pieces (inch)	Mean absorption (mg. per sq. in.)
120	0.081	12.8	0.077	18.1
250	0.080	12.8	0.079	18.5
500	0.083	12.8	0.075	18.3

(c) THE EFFECT OF THE TEMPERATURE OF THE WATER ON ABSORPTION

A thermostatically-controlled, electrically-heated oven was used for this examination. Reliance was placed on convection currents to circulate air within the oven, and the temperature was read on a mercury thermometer protruding through the top, the reading of which was set to 70° C ± 1° C.

A rack of six tubes containing test-pieces was inserted in the oven from back to front. Each test-piece was cut from the same sheet of pressed crepe rubber. Twenty hours later, the temperatures of the water in the tubes were recorded, and were found to have a range of 12° C from front to back. The water absorption of each test-piece was then determined, and large differences were found. The results are shown in Table VII.

TABLE VII

THE EFFECT OF WATER TEMPERATURE ON ABSORPTION

Mean guage of test-piece (inch)	Temperature of water (°C)	Absorption after 20 hours (mg. per sq. in.)
0.077	77	15.8
0.076	74	15.0
0.075	70	13.8
0.074	68	13.3
0.080	67	13.0
0.079	65	12.9

The results in Table VII show that accurate control of the temperature of the water in which the samples are immersed is important; an oven with positive circulation of air, in addition to a good thermostat, is necessary to ensure this. It is desirable to check the temperature of the water as well as that of the air in the oven. The temperature of the water should be 70° C before immersion of the test-pieces.

CALCULATION OF WATER ABSORPTION

In its simple form the calculation of the water absorption per unit area is derived from: $\frac{\text{weight of water absorbed}}{\text{total area of test-piece}}$, but in practice this is modified to take into account shrinkage of the test-piece. All test-pieces show some change of shape during immersion and, as a general rule, this takes the form of a shrinkage in length, with an increase in thickness, except in cases in which the rubber is so prone to oxidation and softening that its own buoyancy stretches it lengthwise when immersed vertically. By the methods of preparation recommended in this

paper, almost all test-pieces retain an approximately rectangular form, and it can be assumed, as an approximation, that the initial surface area of about nine square inches (which includes the area of the edges) is reduced during immersion to about eight square inches. The effective surface area is indefinite, but, for the purposes of calculation, Noble[9] assumes it to be eight square inches for test-pieces about 0.09 inch thick; that is, the loss in effective area due to shrinkage is approximately equal to the original area of the edges. Since it is probable that this procedure is widely used, and because it is admitted that the whole test is one which cannot claim to have great accuracy or give absolute results, it is proposed to adopt eight square inches as the basic surface area for the purpose of calculation when testing crude rubber. Shrinkage is not a problem with vulcanized rubber, and no such broad approximation is necessary.

Having regard to the approximation for shrinkage, small differences in thickness are unimportant but, since the test-pieces prepared by the methods described may have thicknesses up to 0.25 inch in the case of thick sole crepe or other laminated crepe, a correction must be applied to cover such cases.

The method is to adopt a thickness of 0.09 inch as standard, apply a correction for any variation from this thickness, and combine the gain or loss in edge area due to this adjustment with the basic area of eight square inches. Then, if t is the mean gauge of a test-piece, $10(t\text{-}0.09)$ is the excess edge area to be added to the basic area. If W is the weight of water absorbed in milligrams:

$$\text{Absorption} = \frac{W}{8+10(t\text{-}0.09)}$$

$$= \frac{W}{7.1+10t} \text{ mg. per sq. in.}$$

RELIABILITY OF THE EDGE CORRECTION

It was desired to examine experimentally whether the suggested formula gives a reliable correction over a range of thicknesses, and for this purpose sheets of different thickness were prepared from one sample of rubber.

To ensure uniformity, masticated rubber of different thicknesses was used in preference to plied-up crepe. A sample of sole crepe was selected and masticated by passing thirty times through a mill, as previously described, except that after twenty-eight passes the nip was reset. The last two passes determined the thickness of the sheet and, consequently, of the test-piece after pressing. Three tests of each gauge were made under two conditions of immersion, with the results in Table VIII.

Mastication of the rubber produced some distortion during immersion, which is normally avoided by using unmasticated rubber, but from these results it is con-

TABLE VIII

EFFECT OF THICKNESS OF TEST-PIECE ON WATER ABSORPTION

20 hours at 70° C		14 days at 90° F	
Mean gauge of three test-pieces (inch)	Mean absorption of three test-pieces (mg. per sq. in.)	Mean gauge of three test-pieces (inch)	Mean absorption of three test-pieces (mg. per sq. in.)
0.083	15.7	0.080	25.3
0.106	15.9	0.108	25.4
0.133	15.1	0.142	25.8
0.167	16.2	0.159	26.0

sidered that the suggested correction for gauge is adequate to permit comparison between the results obtained with test-pieces of different thickness having regard to the nature of the test.

Having examined the effects of individual factors in the procedure, the following is a summary of the practical details of the test.

THE R.R.I.M. MODIFICATION OF THE BOGGS AND BLAKE IMMERSION TEST

1. To prepare six test-pieces, cut the rubber sample in the shape of a rectangle of approximately $10 \times 4\frac{1}{2}$ inches. If thin crepe, ply-up sufficiently to produce a pressed sheet about 0.1 inch thick.

2. Place between aluminum sheets (size $11 \times 9\frac{1}{2}$ inches), together with an embossed aluminum identification tag.

3. Insert the "sandwich" in a screw-type platen press and hold at 259° F (20 lbs. per sq. in. steam) for 30 minutes.

4. Remove and cool the aluminum sheets under a running tap, without separating them from the rubber.

5. Place in an office-type hand press under light pressure for 24 hours.

6. Remove the rubber and place on parchment paper. Cut test-pieces to a size of 4×1 inches (trimming board or die).

7. Determine the mean gauge of each test-piece by taking about ten readings along the length of each.

8. Attach each test-piece to a glass sinker and immerse in distilled water previously brought to the testing temperature.

9. Keep in a thermostatically-controlled atmosphere for 20 hours at 70° C; and/or for 14 days at 90° F.

Allow the tubes and contents to cool at atmospheric temperature for about half an hour, or cool in any convenient manner to avoid losses when weighing.

11. Remove each test-piece just before weighing; wipe dry with a lintless cloth, and weigh within two minutes.

12. Place in an oven maintained at about 90° C until dry, and reweigh.

13. Calculate the result from the formula:

$$\text{Water absorption in mg. per sq. in. of surface} = \frac{W}{7.1 + 10t}$$

where t is the mean gauge of test-piece in inches, and W is the decrease of weight on drying in milligrams.

TESTING BY IMMERSION OF VULCANIZED RUBBER

Since rubber in the unvulcanized state is rarely called on to perform exacting functions, it is desirable that tests should be made also after vulcanization. For this purpose the mercaptobenzothiazole mixing of the Crude Rubber Committee of the American Chemical Society[17] was selected because it contains a high proportion of rubber, and is also in common use for rubber testing. The formula is:

Rubber	100.0
Mercaptobenzothiazole	0.5
Stearic acid	0.5
Zinc oxide	6.0
Sulfur	3.5
	110.5

The curing temperature is 127° C, and a 60-minutes cure has been selected for comparative routine work in water-absorption testing.

Van Dalfsen[12] did not recommend the use of this mix for water-absorption testing, despite his finding that out of four mixes which he examined ". . . . only in the mixture accelerated by mercaptobenzothiazole did it (purified rubber) behave like normal rubber." The main reasons for his rejection of this mix were, firstly, that the water absorption was affected by changes in the time of vulcanization and, secondly, that the temperature of vulcanization was lower than that commonly used in practice. He chose for test-purposes a 92.5: 7.5 rubber-sulfur mix, but his figures do not indicate that this mix has any particular advantage over the mercaptobenzothiazole mix when testing normal rubber. Using purified rubber in the rubber-sulfur mix, there is less variation in water absorption for different times of cure than in the mercaptobenzothiazole mix, but this is probably due to the comparative ineffectiveness of increased times of cure in a rubber devoid of natural or added accelerators of vulcanization, and it is known that "tight" curing causes a reduction in water absorption. Van Dalfsen's objection to curing at 127° C (20 lbs. per sq. in. steam) is questionable, for much technical curing with mercaptobenzothiazole mixings is done at this temperature, and in any case an equivalent state of cure would be attained by a reduction in time if a higher temperature were used. It could be objected more strongly that a rubber-sulfur mix is not representative of current commercial practice.

As a result of water-absorption tests on a large number of rubber samples cured in the mercaptobenzothiazole mix, it has been found that good agreement with conclusions drawn from tests on crude rubber can be obtained, and the A.C.S. mercaptobenzothiazole mixing is considered to be suitable for comparative testing and routine evaluation.

The Test-Piece

The moulds intended for crude rubber and described under "The Preparation of Test-Pieces" were found to be quite suitable for vulcanized rubber. Sheets are vulcanized in these moulds, and are cut into three strips of size $4\times1\times0.08$ inches. The thickness is 0.08 inch within limits which do not warrant correction (vulcanized rubber does not recover thickness on release of pressure as does unvulcanized rubber).

Calculation of Water Absorption

After immersion, a vulcanized sample does not contract, and the absorption is therefore calculated on the total surface area, which is equal to $(8+10t)$ sq. inches, where t is the gauge in inches. Then, if W is the weight of water absorbed in milligrams:

$$\text{Absorption by vulcanized rubber} = \frac{W}{8+10t}$$

$$= \frac{W}{8.8} \text{ mg. per sq. in.}$$

since t may be considered a constant gauge of 0.08 inch for vulcanized rubber when using the moulds described.

Time of Vulcanization

Using the A.C.S. mercaptobenzothiazole formula, the effect of increasing the time of vulcanization is to cause a reduction in water absorption, as indicated in Table IX.

TABLE IX

EFFECT OF TIME OF VULCANIZATION ON WATER ABSORPTION

Sample No. Time of vulcanization at 127° C (min.)	Mean absorption after immersion for 20 hours at 70° C (mg. per sq. in.)			Mean absorption after immersion for 14 days at 90° F (mg. per sq. in.)		
	81	82	5465	81	82	5465
20	7.1	7.4	10.5	8.0	8.7	14.6
30	6.9	7.6	10.7	7.5	7.7	14.2
40	6.9	7.2	9.5	7.0	7.0	14.2
60	6.1	6.6	9.6	6.4	7.3	13.2
80	6.3	5.9	9.3	5.9	6.4	12.5
100	6.1	6.0	8.9	5.8	6.2	12.4

For routine testing, a single curing time was required, and 60 minutes at 127° C was selected, but a complete evaluation necessitates testing over a range of cures in conjunction with other tests on the vulcanizates.

SUMMARY OF THE METHOD OF EVALUATING THE WATER-ABSORPTION CAPACITY OF VULCANIZED RUBBER

1. Compound the sample, using the American Chemical Society mercaptobenzothiazole mixing. Sheet to a thickness of approximately 0.1 inch, and allow to stand preferably for 24 hours.
2. Lay the sheet in a mould having a cavity depth of 0.08 inch.
3. Vulcanize at 127° C for 60 minutes (or a range of curing times if required).
4. Remove the vulcanized sheet from the mould, cool, and stand for 24 hours.
5. Place on paper and cut three 4×1 inch test-pieces per sample (trimming board or die).
6. Attach each test-piece to a glass sinker, and immerse in distilled water previously brought to the testing temperature.
7. Keep in a thermostatically-controlled atmosphere for 20 hours at 70° C and/or for 14 days at 90° F.
8. Allow the tubes and content to cool at atmospheric temperature for about half an hour, or cool in any convenient manner to avoid losses when weighing.
9. Remove each test-piece just before weighing; wipe dry with a lintless cloth, and weigh within two minutes.
10. Place in an oven maintained at about 90° C until dry, and reweigh.
11. Calculate the result from the formula:

$$\text{Water absorption in mg. per sq. in. of surface} = \frac{W}{8.8}$$

where W is the decrease of weight on drying, in milligrams.

ACKNOWLEDGMENT

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TRILINEAR COMPOUNDING *

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Trilinear compounding enables the factory compounder to select the particular rubber or synthetic rubber composition that will have the physical properties specified. It saves time in eliminating trial-and-error methods of compounding. Briefly, charts of this type actually tell the ratio of rubber (or synthetic rubber): filler: softener, and similar charts can be made to show other systems.

Every rubber chemist knows that there are two primary methods of altering the physical properties of vulcanized rubber and synthetic rubber—chemical and physical. The former is controlled by antioxidants, accelerators, activators, and other curing agents; the latter is controlled by fillers and softeners. This discussion deals with the physical methods that are applicable after factors influencing rate and state of cure have been fixed.

This method of compounding has been named "trilinear compounding". It employs charts which show the effects of varying three ingredients in a compound. In other words, it deals with a compound as a unit which is divisible into three parts. Trilinear compounding is not new; it is used regularly in the paint and plastics industry. Undoubtedly, several rubber chemists have used it in connection with compounding by chemical means and in many special applications, but its recourse to fillers and softeners is believed to be new to most rubber chemists.

DESCRIPTION OF CHART

A trilinear coördinate chart, Figure 1, is the basis of trilinear compounding. The use of these charts comes from a simple function of plane geometry. The sum of the perpendicular distances from any point on the surface of an equilateral triangle to the three sides is equal to the height of the triangle.

However, the charts can be used in an easier and more practical manner than geometric interpretation. In Figure 1, the key points are identified by assigned letters. Each apex, A, B and C, represents 100 per cent of a definite material. In compounding polymers, one of the materials is designated as the base, and it usually contains more than one ingredient. The three components must be quoted in identical units, and they are designated on a volume basis so that all possible combinations (with respect to actual weight) are included.

In the charts which follow, the base is Neoprene Type-GN plus the necessary modifying agents required for vulcanization and processing. The point A will represent 100 per cent by volume of this Neoprene base. The points B and C will represent 100 per cent by volume of any two other components used to complete a compound. Each base line represents 0 per cent by volume of the material represented by the opposite apex. The perpendicular distances from any base line to the opposite apex is divided into 10 units for convenience in stating percentage by volume composition. For example, the point G, where the lines AF, BD and EC intersect, represents a composition containing 33⅓ per cent

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by volume of each of the three components. However, any point within the triangle represents 100 parts by volume of the whole composition. Point H would be 50 per cent of component A, 25 per cent of component B and 25 per cent of component C, all of which are on a volume basis.

These charts are of great value when studying the properties of compositions, because the effects of varying the composition can be followed. Areas are thus found on the trilinear chart that will represent compositions producing a specific range of properties. Existing or new data can be used to construct a chart. In the former case, the points representing compositions that have been tested are located, and then the data are transposed to the respective points. Thus, a range of properties with respect to composition is plotted on the graph. Conversely, a new chart can be constructed by first spotting compositions on a graph and then testing those compositions. This latter method probably has the largest general use.

USE OF TRILINEAR CHARTS

As previously indicated, these charts may be applied to rubber or synthetic rubber. The number of charts that can be constructed is almost infinite. Neoprene was used to develop this means of compounding because such a base is fixed more than a rubber base. Two trilinear charts will be described.

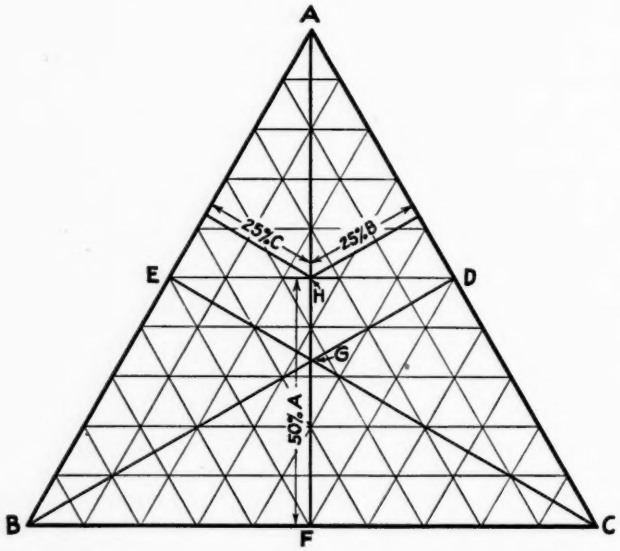

FIG. 1.

The first three-phase system, Figure 2, includes Neoprene Type-GN base, Neophax-A, and Circo light process oil. The three bisecting axes of the equilateral triangle of the chart, divided into 100 equal parts, each represent one volume of their respective components. The AF axis refers to Neoprene base, the CE axis refers to Circo Light Process oil, and the BD axis refers to Neophax-A.

Contours or curves plotted on Figure 2 classify the compositions represented by the graph according to their hardness and swelling in kerosene (2 days at 100° C)[1]. The contours labeled by circled figures refer to swelling; the others refer to hardness. It will be noted that swelling is plotted in 10 per cent volume increase ranges, and hardness in 4 point ranges of the Shore durometer. Therefore, any "square shaped" area describes the compositions of that area with respect to hardness and swelling.

For purposes of illustration, let it be assumed that a compounder desires the formula of a soft Neoprene stock, having a hardness of 20 to 25, and a volume increase of 90 to 100 per cent in kerosene. He selects point R (indicated on Figure 2), and then proceeds to determine the formula of this composition. He reads from the chart that Compound R contains:

46.15%	Neoprene base by volume $= N$
41.95%	Neophax-A by volume $= X$
11.90%	Circo Process oil by volume $= Y$
100.00%	compound by volume

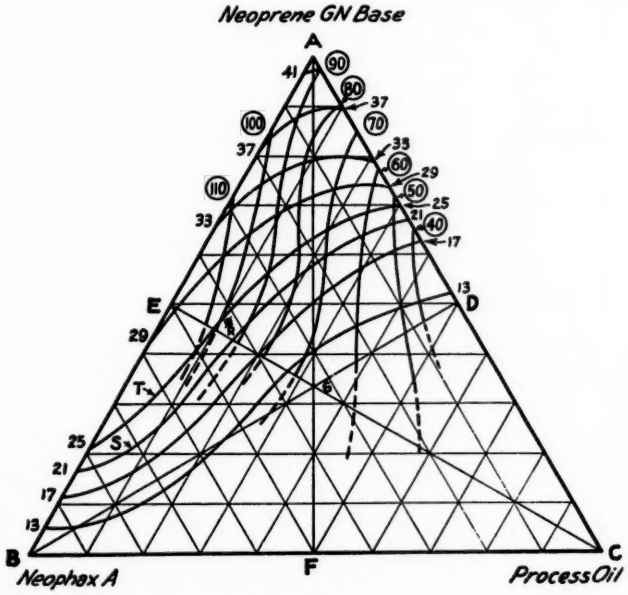

FIG. 2.—Volume increase in kerosene indicated by figures in circles (per cent); Shore durometer hardness indicated by other figures.

It is obvious that the sum of N, X, and Y volumes is equal to 100 volumes of compound. However, since all factory compounding is done on a weight basis, he must transform this volume composition to a practical formula. From the original data used in constructing the chart, it is known that the Neoprene base of the graph is a complete gum-stock, including all ingredients that affect physical properties by chemical reaction or catalysis. This base bum-stock has already been adjusted to produce a good state of cure in 40 minutes at 287° F. The formula can now be written:

		Parts by weight
Neoprene base ($N = 46.15\%$ by volume)	Neoprene Type-GN (sp. grav. 1.25)	100.0
	Latac (sp. grav. 1.17)	0.375
	Stearic acid (sp. grav. 0.92)	0.5
	Neozone-A (sp. grav. 1.18)	2.0
	Extra-light calcined magnesia (sp. grav. 3.20)	4.0
	Zinc oxide (sp. grav. 5.57)	5.0
		111.875

Neophax-A ($X = 41.95\%$ by volume)	= Neophax-A (sp. grav. 1.04)	x
Circo Process oil ($Y = 11.9\%$ by volume)	= Circo Process oil (sp. grav. 0.92)	y
Compound ($N + X + Y = 100\%$ by volume)	= Weight of whole compound $- 111.875 + x + y$	

The weight of Neophax-A and Circo Process oil must be calculated. This can easily be done by substituting the values of N, X, and Y in simple equations and solving for x (weight of Neophax) and y (weight of Circo oil). The constants in the equations are actually conversion factors based on the specific gravities of the three components of the chart. These constants must be determined for each filler or softener. In the systems described in this paper, the constant for any diluent=specific gravity of diluent (filler or softener) x specific volume of Neoprene base (84.71). The specific volume of the Neoprene base is determined by dividing its weight (111.875) by its specific gravity (1.282).

$$y = \frac{Y}{N} \times \text{constant} \qquad x = \frac{X}{N} \times \text{constant}$$

$$= \frac{11.9}{46.15} \times 77.9 \qquad = \frac{41.95}{46.15} \times 88.1$$

$= 20$ parts by weight Process oil $\qquad = 80$ parts by weight Neophax-A

Therefore, by substituting the values of x and y just calculated in the formula shown, the completed formula of this compound, R, having the selected properties, becomes:

COMPOUND R

Neoprene Type-GN	100.0
Latac	0.375
Stearic acid	0.5
Neozone-A	2.0
Extra-light calcined magnesia	4.0
Neophax-A	80.0
Circo Process oil	20.0
Zinc oxide	5.0

In general, Figure 2 is a compounding guide for stocks having a Shore Durometer hardness range of 42 to 0. It was constructed from the data in Table I. The hardness values of the compounds in Table I plotted on the chart and contour lines were drawn to show areas in which all compositions have the same hardness. For example, the hardness of the vulcanizate of any compound within the area between the contours S and T is 21 to 25, regardless of the ratio; Neoprene base:Neophax:oil. Compound R, just discussed, is within this area and has a hardness of 23.

TABLE I

PHYSICAL PROPERTIES OF NEOPRENE TYPE-GN BASE, NEOPHAX-A AND CIRCO PROCESS OIL COMPOSITIONS, CURED 40 MINUTES AT 287° F

(40 pounds steam pressure per sq. in.)

Neophax-A W/N[1]	Process oil W/N[1]	Volume composition: Per cent Neoprene base	Volume composition: Per cent Neophax-A	Volume composition: Per cent Process oil	Modulus at 500% elongation	Tensile strength	Elongation	Shore hardness	Volume increase kerosene 2 days at 100° C
—	—	100.00	—	—	475	3,500	850	42	93.7
—	10	88.80	—	11.2	375	2,675	920	36	76.7
—	20	79.60	—	20.4	225	2,200	930	31	62.4
10	—	89.78	10.22	—	525	2,550	850	39	97.0
20	—	81.44	18.56	—	575	2,300	900	37	103.9
40	—	68.68	31.32	—	725	1,525	825	34 +	111.3
80	—	52.35	47.65	—	725	825	640	31	131.2
20	10	73.70	16.80	9.5	425	1,750	870	31	81.9
20	20	67.40	15.30	17.3	325	1,550	920	27	71.8
40	20	58.40	26.60	15.0	425	1,175	850	26	87.7
80	10	49.10	44.60	6.3	650	925	740	27	121.4
80[2]	20	46.15	41.95	11.9	525	800	760	23	96.0
80	40	41.20	37.60	21.2	350	575	750	17	78.0
130	—	40.40	59.60	—	—	750	420	29	124.0
—	—	—	100.00	—	—	—	—	11	dissolved
15	50	55.10	9.40	35.5	175	1,150	1,020	16	52.7
90	80	32.80	33.50	33.7	225	350	650	10	65.3
160	40	30.00	54.60	15.4	—	450	410	19	79.5
35	90	37.40	14.90	47.7	125	600	1,020	7	50.0
350	—	20.10	79.90	—	—	275	210	25	134.0
50	50	45.20	25.70	29.1	275	725	915	16	77.1

Parts by weight per 100 parts of Neoprene.
Compound R (see text).

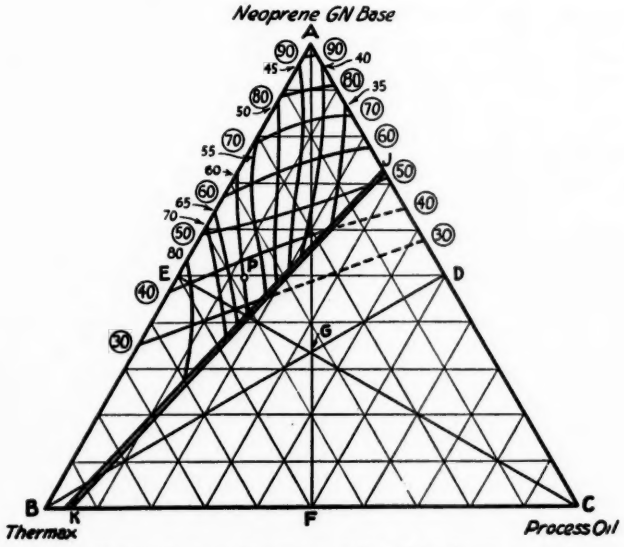

FIG. 3.—Volume increase in kerosene indicated by figures in circles (per cent); Shore durometer hardness indicated by other figures.

In addition to Durometer hardness, other contours show the resistance to swelling in kerosene of these soft Neoprene compositions. The direction assumed by these contours is more or less perpendicular to the hardness curves, and a network of "square shaped" areas is formed. These areas each represent a group of compounds whose hardness and volume increase in kerosene is within the respective ranges shown. In this chart, the swelling contours are not extended to the base of the triangle because compositions of Neophax and carbon black alone are not practical.

TABLE II

PHYSICAL PROPERTIES OF NEOPRENE TYPE-GN BASE—THERMAX—CIRCO PROCESS OIL COMPOSITIONS, CURED 40 MINUTES AT 287° F

(40 pounds steam pressure per sq. in.)

Thermax W/N[1]	Process oil W/N[1]	Volume composition: Per cent Neoprene base	Volume composition: Per cent Thermax	Volume composition: Per cent Process oil	Modulus at 500%	Tensile strength	Elongation	Shore hardness	Volume increase kerosene 2 days at 100° C
—	—	100.0	—	—	475	3,500	850	42	93.7
28.8	—	84.2	15.8	—	1,525	2,200	740	52	74.9
28.8	20.0	69.15	13.09	17.76	825	2,325	930	38	57.0
57.6	—	73.25	26.75	—	1,900	1,950	520	59	67.3
57.6	10.0	66.4	25.1	8.5	1,675	2,000	715	52	57.4
57.6	20.0	61.1	23.15	15.75	1,275	1,950	810	45	46.7
86.4	—	63.8	36.2	—	—	1,875	415	65	57.1
86.4	10.0	59.0	33.4	7.6	1,825	1,825	500	56	48.3
115.2	—	57.0	43.0	—	—	1,850	250	76	47.1
115.2	10.0	53.0	40.2	6.7	—	1,900	335	67	41.6
115.2[2]	20.0	49.65	37.6	12.75	—	1,875	400	60	36.7
172.8	—	46.8	53.2	—	—	1,850	170	87	40.1
—	10.0	88.8	—	11.2	375	2,675	920	36	76.7
—	20.0	79.6	—	20.4	225	2,200	930	31	62.4
106.5	23.3	50.0	35.0	15.0	—	1,475	395	56	33.1
29.5	14.8	75.0	12.5	12.5	925	1,900	815	42	56.8
9.5	14.6	80.0	5.0	15.0	400	1,000	675	40	63.1

[1] Parts by weight per 100 parts of Neoprene.
[2] Compound P (see text).

Additional contours can be drawn or additional areas indicated on Figure 2 which will classify compositions with respect to other physical properties, such as modulus, tensile strength, permanent set, and resilience.

The second three-phase system used to illustrate trilinear compounding is based on compositions containing Neoprene base, Thermax, and Circo Process oil. This system is shown in Figure 3, and is based on the data in Table II. The principles just described in discussing the Neophax-A, Circo Process oil and Neoprene Type-GN base system also apply to this system, which is: Thermax, Circo Process oil, and Neoprene Type-GN base. In this chart, hardness contours assume a vertical direction because the stocks become harder as the filler content increases. In constructing these hardness contours, it was necessary to assume that the hardness of Thermax (s. g. 1.80) alone is 100 and process oil alone is 0.

The formulas for transcribing volume composition of Neoprene diluents to parts by weight per 100 parts by weight of Neoprene are:

$$\text{Thermax} = t = \frac{T}{N} \times \text{constant}$$
$$= \frac{T}{N} \times 152$$
$$\text{Circo Process Oil} = y = \frac{Y}{N} \times \text{constant}$$
$$= \frac{Y}{N} \times 77.9$$

The point P on the trilinear chart of Figure 3 represents a compound having a Shore hardness of 60, and contains the following volume composition:

Neoprene base	$49.65\% = N$
Thermax	$37.60\% = T$
Process oil	$12.75\% = Y$

Upon substituting these values in the equations, the formula of the stock is derived:

COMPOUND P

Neoprene Type-GN	100.0
Latac	0.375
Stearic acid	0.5
Neozone-A	2.0
Extra-light calcined magnesia	4.0
Thermax	115.2 *
Process oil	20.0
Zinc oxide	5.0

* 80 vols. per 100 vols. Neoprene.

In Figure 3, the horizontal contours serve to classify the compositions with respect to their volume increase in kerosene over a two-day period at 100° C. These contours are based on interpolations made from the volume increased values of several compounds. Compound P should swell between 30 and 40 per cent; actually it swelled 36.7 per cent.

These volume-increase contours constitute an important relationship that is common to any filler used with this Neoprene base and process oil. Fraser and Catton[2] showed that the swelling of any Neoprene compound by oil was independent of the filler used, but was dependent on the volume dilution of the Neoprene by filler. Therefore, the volume-increase contours apply not only to Thermax but also to other fillers when substituted for Thermax on an equal volume basis.

The line JK is very significant because it is the bloom point of compositions of this system. Any composition represented by a point below this line will exude oil after cure. Compositions represented by points above this line do not exude oil. This bloom point designation in Figure 3 applies only to this system, and the blooming boundaries of other systems must be determined individually.

Other physical properties, which are indicated in an approximate manner by the hardness areas, can be shown accurately by contours. Modulus will be higher while elongation, compression set, and resilience will be lower in those areas representing harder compounds. In this system, changes in tensile strength from

one composition to another follow a very narrow range. This is a characteristic of Neoprene compounds containing soft carbon black. However, extreme loading of soft carbon black and (or) process oil reduce the tensile strength.

TYPICAL APPLICATIONS AND SCOPE OF SYSTEM

It has already been pointed out that a trilinear chart can be used to eliminate guess work and to save the time of the factory compounder. From it one can select the composition that will come nearest to duplicating desired physical properties. In this respect, it should be of value in duplicating the properties of competitive samples. The two systems discussed are not the only charts that can be constructed, nor do they show all of the physical properties that could be plotted. Other examples of how trilinear compounding may be applied are summarized:

1. Compounds of definite swelling resistance can be selected with respect to hardness.

2. Compounds of definite hardness and swelling resistance can be selected with respect to approximate modulus, tensile strength, permanent set, and resilience. These physical properties could be determined more accurately by plotting contours representative of particular properties.

3. The swelling resistance of compounds containing another filler substituted for soft carbon black on an equal volume basis can be determined directly from the chart.

4. The swelling of the compositions in another oil can be determined by conversion factors. The volume increase in kerosene under specific conditions is shown. Fraser[3] showed that the swelling of a given Neoprene composition depends on the viscosity-gravity constant or the aniline point of an oil. For example, oils having a low aniline point swell Neoprene compounds most; therefore, by analogy an oil having a higher aniline point than kerosene used would not swell the Neoprene to so great an extent. The effects of temperature and time are independent factors, and swelling is proportional to time and temperature.

5. Whether or not a Neoprene-Thermax-process oil composition exudes oil can be readily determined from the location of the point representing the compound. If above the bloom line, it will not exude oil.

6. The number of three component systems that can be charted is infinite, but for all practical purposes, a few will answer most requirements. All of the systems would be made up of rubber or synthetic rubber bases, filler and softener, or any combination of the three components. These are six key systems:

a. Base stock:filler:softener
b. Base stock:filler:filler
c. Base stock:softener:softener
d. Base stock No. 1:Base stock No. 2:filler
e. Base stock No. 1:Base stock No. 2:softener
f. Base stock No. 1:Base stock No. 2:Base stock No. 3

It will be noted that any key system must contain a base stock made from rubber or synthetic rubber. Furthermore, any one component can be subdivided within itself if such a subdivision remains a constant, *e.g.*, a filler may refer to a 50 per cent by weight blend of two types of carbon black.

7. It is believed that trilinear charts can be used to plot such properties as tear resistance, water resistance, abrasion resistance, and many others.

LIMITATIONS

Many charts may be constructed showing all the various relationships desired. The only limitation is that one chart cannot be constructed to include all possible combinations. This system of compounding simplifies itself as its use is extended, because conversion factors can be calculated that will refer a given compound in part or whole to another system. These conversion factors would apply particularly to the substitution of fillers and softeners for one another.

Variations in the rubber or synthetic rubber base cannot be made, because each of the three components must have a constant composition within a given chart. Variations of the curing agents, accelerators, etc., of the base must be accounted for separately. However, after a composition has been selected from a point, the properties of this composition can then be adjusted by varying the components of the rubber or synthetic rubber base.

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EQUIPMENT FOR ACCELERATED LIGHT-AGING OF RUBBER, AND METHODS OF EVALUATION OF ULTRAVIOLET LIGHT AND SUNLIGHT *

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In connection with the development of a suitable light-aging test for evaluating the light-aging properties of rubber, plastics, dyed fabrics, and paints, a considerable amount of research work and literature search was undertaken. The purpose of this article is to make readily available these data to facilitate additional work in the evaluation of the weathering and light-aging of the above-mentioned materials. It is intended to present these data in a somewhat informal style, and to set forth not only the successful experiment, but also those tests which have been disproved as being either impracticable or not applicable to the particular material under investigation.

Most of the work has been done in connection with rubber compounds and synthetic rubber-like materials, with the primary purpose of differentiating between satisfactory and unsatisfactory materials from the standpoint of light-aging and weathering resistance. However, there is a secondary purpose which, at present writing, is far more important and outweighs the mere procurement of material, that is, its use in improving rubberlike compounds themselves.

Several years ago a standardization program was being worked out for evaluating sunlight resistance by means of exposure to natural sunlight. A questionnaire was sent to various rubber manufacturers and interested laboratories. A tabulation of the data indicated that a number of the manufacturers were experimenting with the idea of evolving a method which would more rapidly evaluate this property and differentiate between various gradations of light-aging resistance. The results of the questionnaire indicated further that there was no uniformity in the methods pursued or in the manner in which samples were exposed. For the purpose of including a light-aging requirement in various government specifications, it was thought desirable to determine if standardization of some method could be effected. The use of mercury quartz lamps to obtain accelerated results of aging had been so unsatisfactory, insofar as correlation with actual sunlight exposure was concerned, that these attempts were discontinued. Before standardization of equipment and test procedure could logically be pursued, it was essential to select some equipment which would give a reasonably constant source of light, and to select some method of measuring the intensity and range of the ultra violet light used.

A comprehensive literature search of known methods of evaluating the intensity of ultraviolet light disclosed that a number of satisfactory methods were available which would estimate the total dosage of ultraviolet light to which rubber or other materials would be subjected. There were certain difficulties encountered in making this selection. One of them was that, to determine light-aging resistance of

* Reprinted from the *India Rubber World*, Vol. 105, No. 2, pages 143-146, November 1, 1941; No. 3, pages 264-268, December 1, 1941.

various types of rubbers, it would be desirable to determine the sensitivity curve, just as a sensitivity curve was developed for the erythemal response or sunburn effect on the human skin. Variation of the range of ultraviolet light produces markedly different effect on the rubber samples.

The possibilities and extremes of errors in the determination which may come up in connection with correlation of sunlight and ultraviolet light can best be illustrated by a theoretical example. Suppose one has an instrument (it does not matter whether it utilizes a photoelectric cell or a photosensitive chemical solution) which is sensitive over the range of from 2,750 to 4,000 Angstrom units; then all light within this range will produce a change proportional to the intensity of the light over all wave lengths within this range. Suppose now that one has two sources of light, one of which, emitting light over a range of wave lengths between 2,750 and 3,000, is called A. Another lamp, emitting light over a range of wave lengths between 2,950 and 3,200 Angstrom units, will be called B. When measured with the instrument mentioned above, A shows a certain deterioration of uranyl oxalate solution; for example, equivalent to 150 milligrams per square decimeter per hour, and lamp B shows a similar deterioration of 150 milligrams per square decimeter per hour. Let it be assumed that identical samples of a material are exposed simultaneously to the effect of lamp A and lamp B for an equal length of time. The deterioration of the tensile strength is measured after such exposure. In the case of lamp A, the deterioration is assumed to be equivalent to 75 per cent of the original tensile strength of the material; whereas the deterioration shown by the same compound in lamp B is only 25 per cent. According to the intensity measurement made by the instrument, the two lamps should have shown approximately equivalent amounts of deterioration, but it so happened that the wave length light in lamp B was essentially outside of the range of sensitivity which would effect the deterioration of the particular rubber.

If the wave-length light to which the rubber was sensitive is also found in sunlight, then one would expect to get fairly close correlation between sunlight deterioration and the deterioration caused by the ultraviolet light lamp. Of course this is an extreme case, and has not been experienced in rubber testing using the flaming-arc light unit, but may be an explanation for the poor correlation which has been reported in certain instances of experiments made to correlate sunlight deterioration and ultraviolet light deterioration caused by certain types of the ultraviolet-aging lamps. Inasmuch as this difficulty is inherent in the material itself and depends on the range of the ultraviolet-aging lamp, this objection would present itself, regardless of the type of equipment used to measure ultraviolet light intensity. A relatively narrow range of ultraviolet should be selected for this purpose.

Earlier experiments seem to indicate that it would be possible to select definitely a certain range of ultraviolet light between 2,950 and 3,350 Angstrom units which would be responsible for the major portion of rubber deterioration. As data began to accumulate, however, it became apparent that light of the same intensity and the same range affected different compounds to a different degree. Whereas in some instances reasonably good correlation with deterioration obtained with actual sunlight was secured, in other cases deterioration was not of the same magnitude or even in the same order as the deterioration obtained with natural sunlight. Thus, for example, one of the synthetic rubbers was found to undergo a lesser decrease in tensile strength when subjected to accelerated ultraviolet light than the tensile strength deterioration when subjected to natural light. On the other hand the extent of cracking and crazing of the surface was in the reverse

order. In other words, the problem of light-aging is not only an important one, but is a very active one. Only by the whole-hearted coöperation of the manufacturers of the rubber industry and the consumers of rubber articles, both private and government agencies, can final solution of this problem be evolved.

The present national emergency makes it imperative to utilize every known means of getting more life and more service out of rubber and rubberlike materials. The inclusion of a light-aging test in all specifications for rubber articles

FIG. 1.—Diagram of Machlett type of dispensing burette.

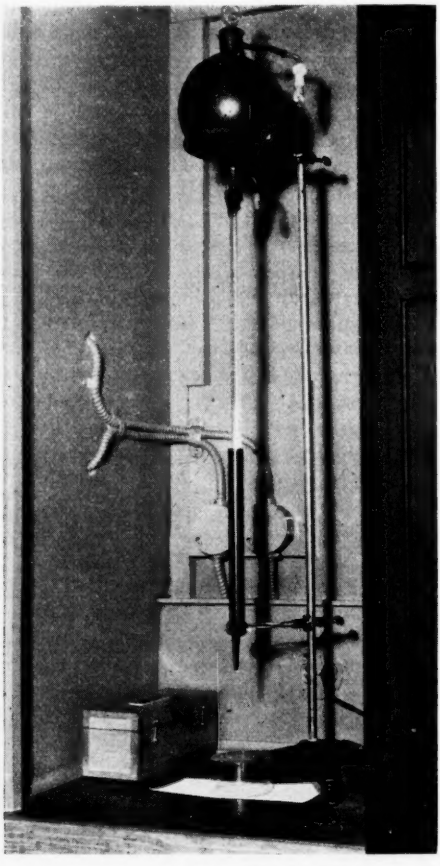


FIG. 2.—Dispensing burette for actinometer solution.

which are used under conditions where they are subject to weathering and sunlight will, it is believed, serve to do this very thing.

If we can make a piece of hose last two and one-half years, where formerly it lasted only a year and a half, or year and three-quarters, we have saved that much rubber, and are to that extent progressing in the conservation of strategic materials.

Let us cite a concrete example. Soft rubber gasket stock is extensively used as a gasket in airports, aboard commercial and naval vessels. When the airports

are left open, this rubber gasket is exposed to the direct sunlight and to reflected sunlight from the water surface. Deterioration under these conditions is very rapid. In spite of the fact that the compound used in this type of gasket is very high-grade medium soft rubber, experiments carried out within the last year indicate that the life of this particular gasket material may be increased when properly protected by the inclusion of materials improving this sunlight resistance. Since many thousands of pounds of this material are bought for this one purpose alone, it may readily be seen how effectively conservation of rubber and rubberlike materials may be carried out in this manner.

The selection of suitable equipment for the initial experimental purposes was a problem. The apparatus in which accelerated aging was to be carried out had to be of sufficient size so that a relatively large number of samples could be accommodated simultaneously. As the susceptibility curve of the various rubbers was not known. The apparatus was required to be sufficiently flexible so that both the intensity and the range of the ultraviolet light could be shifted at will. The action had to be automatic and require only a reasonable amount of attention on the part of personnel.

These several desirable properties were incorporated in a flaming-arc type of carbon lamp, in which carbons of any desired type or spectral distribution could be burned and in which the samples could be exposed to the light either directly or after having passed through suitable glass or Corex-D filters. Originally the tests were carried out with light filtered through Corex-D filter glass but, with the ever-increasing desire for speed in testing, it became evident that some sacrifice might have to be made in the degree of correlation in the accelerated light-aging and natural-light aging to reduce the time of exposure. By proper selection of carbons to obtain a range of ultraviolet light similar to natural sunlight, it was found that apparently good correlation may be obtained in this "super-accelerated" aging test. Originally this test was intended as a rough approximation to be used only in research investigations. For specification purposes, a test procedure was developed which called for exposure of longer duration to ultraviolet light filtered through Corex-D filter. Fortunately, however, the correlation with natural sunlight was sufficiently satisfactory to warrant inclusion of this test procedure in hose-cover stock specifications and other rubber materials which are exposed in normal service to weathering and sunlight. The cost of testing is decreased to between 10 to 20 per cent of the long-time exposure test.

There is one objection to this super-accelerated test, that is, that variation in the intensity in the light-aging equipment is correspondingly magnified. In other words, in a 500-hour test approximately 60 sets of carbons would be used, and variations which cause intensity fluctuations would be balanced out. However, when the entire test is only 50 hours, relatively slight variations in intensity of the equipment become magnified proportionately.

Earlier in the article we mentioned the desirability of having some means of keeping a constant check on ultraviolet light intensity. This is particularly important when it is desired to check the equipment of one laboratory with that of another, or where it is essential to conduct umpire tests. If the question of cost of equipment did not enter into the picture, perhaps the simplest method would be the use of a Taylor recording photoelectrometer. Its cost used to be approximately $3,000, and it is the writers' understanding that the cost of this material has increased in recent months. Rentchler, Brackett and Kuper have developed an ingenious photoelectric integrating meter for ultraviolet radiation. Investigation of this type of equipment indicated that this apparatus was designed to cover a range from 2,950 to 3,200 Angstrom units. By using a Thorium photo-

cell, the sensitivity range can be modified to cover a range of 2,700 to 3,600 Angstrom units. The maximum counting speed is one "click" per second. This is fast enough for natural-sunlight aging, as summer sun gives only about one count or click every three seconds. For strong ultraviolet light lamps it would not work fast enough, unless the instrument were used at a greater distance than the distance between light and the specimens aged.

In the bibliography, references are given to a number of other methods which were investigated. However, largely on the recommendation of W. W. Coblentz,

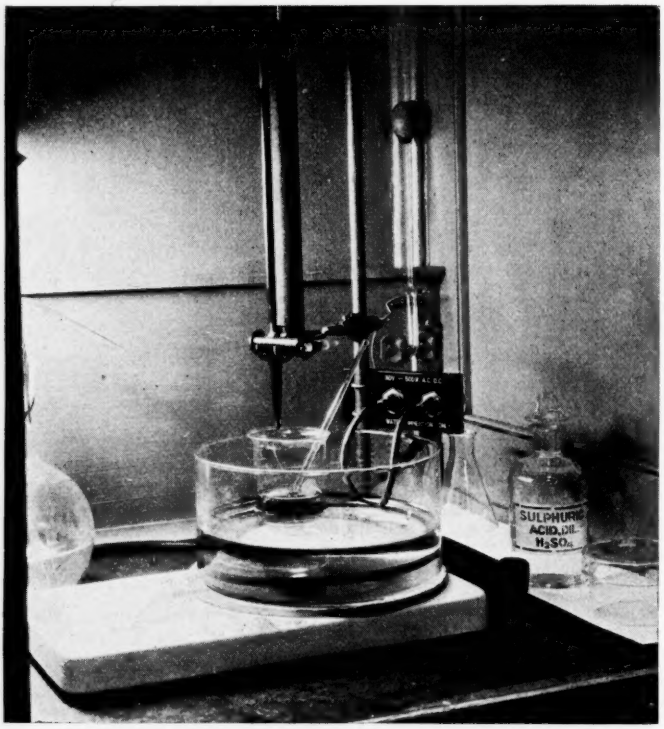


FIG. 3.—Titration apparatus for evaluating solution.

of the National Bureau of Standards, the uranyl oxalate method was decided on as most nearly meeting the following requirements:

(1) The apparatus should accurately determine the intensity of ultraviolet light over the range generally found in sunlight, and preferably below 2,750 Angstrom units.

(2) The apparatus should not require standardization, except at rare intervals.

(3) The equipment should be simple enough for any technically trained operator not especially versed in this subject to take readings.

(4) The apparatus for the equipment should be sufficiently inexpensive so all laboratories using ultraviolet light accelerated aging tests can avail themselves of this method to check intensity.

(5) It is desirable that the apparatus be capable of measurements over a relatively extended period of time so that the cumulative effect of light exposure can be determined.

(6) The time required for making determinations should be as short as possible.

This uranyl oxalate actinometer method, which is briefly described in Federal Specification ZZ-R-601a, is carried out as follows:

The actinometer solution consists of a 0.050 molal concentration of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$), *i.e.*, 6.30 grams per liter and a 0.0100 molal concentration of uranyl sulfate ($UO_2SO_4 \cdot 3H_2O$), *i.e.*, 4.20 grams per liter. The evaluating solution is a 0.100 normal (oxidation equivalent) potassium permanganate ($KMnO_4$) solution, containing 3.16 grams per liter.

The above solutions may be prepared in ordinary diffused light, but should be stored in darkness, immediately after preparation, and should be kept in darkness, until used. The solution of potassium permanganate, before use, should be allowed to stand for one week and then filtered through a $\frac{1}{8}$-inch thickness of fibrous glass filter cloth. The automatic dispensing burette, shown in Figure 1 and 2, is suitable for storing and dispensing the solutions when the reservoir and connecting tubes have been heavily coated with black enamel to exclude light.

The actinometer solutions are titrated against the evaluating solution when fresh lots of either solution are prepared, or when either solution has stood more than 60 days. The titration should be made by taking an accurately measured 45- to 50-cc. portion of the actinometer solution in a 200-cc. tall-form beaker, diluting it with 20 to 25 cc. of distilled water, acidifying with 5 cc. of dilute (1 to 3) sulfuric acid, and heating to approximately 95° C in a lightproof water bath. The beaker containing the solution, on reaching 95° C, should then be immediately transferred to an open glass water bath, also heated to 95° C and resting on a flat white glass base (see Figure 3). The evaluating solution should be added, with stirring, until an orange color is obtained, which persists for at least 30 seconds. The titration should be conducted in such a way that the volumes of solutions used are precise to within plus or minus 0.05-cc. The evaluating solution (potassium permanganate) should be standardized against sodium oxalate in the usual way, with such precautions that its strength is known with an accuracy of at least plus or minus 0.1 per cent. This strength is expressed in terms of the number of milligrams of anhydrous oxalic acid to which one cc. of the solution is equivalent.

The intensity of radiation is measured in terms of the milligrams of oxalic acid decomposed per square decimeter per minute, and the quantity of radiation in any given time is measured in terms of the milligrams of oxalic acid decomposed per square decimeter. The actinometer cell is filled with a precisely measured quantity of uranyl oxylate solution, placed in the holder and exposed to the radiation of the ultraviolet light unit or natural sunlight under the same conditions as the specimens under test. The distance from light source to actinometer cell should be adjusted as closely as possible to be the same as that between the light source and the surface of the test sample, because the intensity of the radiation varies as the square of the distance.

The cell is protected from light, except during the actual exposure period. After exposure, the solution from the cell should be titrated against the evaluating solution by the procedure outlined above for standardization; the quantity of the evaluating solution required is designated as V_1. A similar titration is made on a volume of actinometer solution equal within plus or minus 0.05 cc. to that which was exposed in the cell; the quantity of the evaluating solution required is designated as V_2. The quantity of oxalic acid, in milligrams, decomposed by the radiation to which the cell was subjected is given by the relation:

$$Q = a(V_2 - V_1)$$

where a is the number of milligrams of oxalic acid equivalent to 1 cc. of the evaluating solution. V_1 should be not more than 90 nor less than 70 per cent of V_2; in other words, decomposition should be between 10 and 30 per cent.

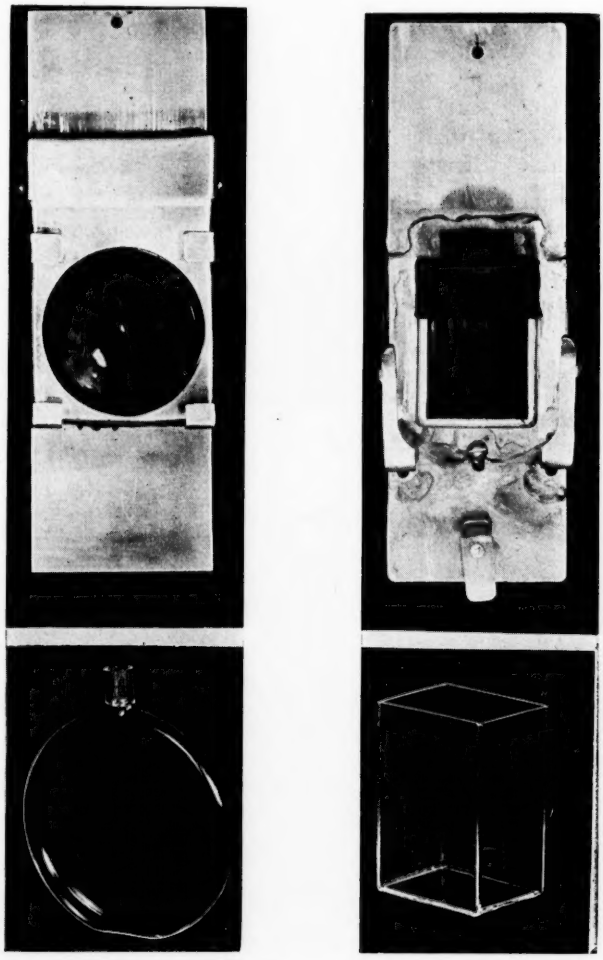
The quantity or dosage of radiation is expressed as: $\frac{Q}{A}$, and the intensity of radiation as $\frac{Q}{At}$, where A is the area of the cell, in square decimeters, and t the time of exposure in minutes.

The material for test is in the form of strips moulded or buffed to a uniform thickness of not less than 0.07- or more than 0.08-inch. These strips are stretched to an elongation of 20 per cent (except as will be noted) by means of a suitable frame, and mounted so as to receive the radiation from the ultraviolet light source. The temperature of the air in the vicinity of the specimens being irradiated should be kept at 50° plus or minus 5° C, by controlling the temperature of the room and the ventilation of the space surrounding the specimens. The dosage of radiation varies with different types of rubbers or synthetic rubber, but is measured by means of the actinometer solution and cell described above. With new materials, measurement of radiation is made at the beginning and the end of each run, and at intervals of not more than 24 hours during the run. Immediately at the end of the exposure period, the strips are examined by means of a binocular microscope for cracking and checking. They are released, and allowed to stand for at least 16 hours, after which dumbbell specimens are prepared, and measurements made of tensile strength and ultimate elongation. Similar measurements should be made of specimens which were not exposed to the radiation to determine changes in tensile strength and percentage elongation.

A number of photographs are included to show the type of apparatus which has been found suitable. In the development of this method, a number of modifications of procedure were tried, such as the use of stirring equipment to keep the action of actinometric solution of uniform concentration throughout the absorption period. A number of these modifications are indicated in the accompanying photographs, and are included solely for the purpose of avoiding duplication of effort, because these methods have been tried and found to complicate unnecessarily the equipment; in fact, to vitiate some of the desirable points listed above.

Figure 1 indicates a type of burette which has been found to be particularly suitable in the titration of the uranyl oxalate solution with potassium permanganate. Figure 2 illustrates this type of burette in a dark-room closet used in titrating the actinometer solution. A similar burette is used for the permanganate solution. The equipment found suitable for maintaining the actinometer solution at the desired temperature during titration is shown in Figure 3. Figure 4 shows the rectangular Forbes cell and holder, and the round Fisher actinometric cell and holder, which contain the sensitive solution. The holders are constructed of aluminum or other suitable lightweight metal. Except for the exposed glass-surface, the interior of the holder is painted black to avoid transmission of light, except through the carefully measured surface of the actinometric cell. Figure 5 shows a holder for the Fisher cell mounted in the revolving frame of the light aging unit. Various attempts have been made to determine if stirring of the actinometric solution during exposure to ultraviolet light would give more consistent results. An apparatus of this type, with an air-driven stirrer, is shown in Figure 6, in its unassembled form, and in Figure 7 with the various parts

assembled. Tests, however, indicated that stirring of the actinometric solution is not necessary when a thin layer of solution is exposed to the light, as with the round Fisher cell. If it is desired to measure the comparative intensity and uniformity of different lights having the same spectral distribution, it is satisfactory to use Fisher cells. A specimen holder suitable for exposure is shown in Figure 8.



Round or Fisher actinometric cell and holder.

FIG. 4

Rectangular Forbes actinometric cell and holder.

The dimensions of a suitable holder are shown in Figure 9. Comparative tests between Eveready X-1 Unit, an Atlas Weather-Ometer, and Atlas Fade-Ometer were made, using the uranyl oxalate actinometer.

The distance between the light source and the specimen or actinometric cell for this equipment is shown in Table I.

An interesting experiment was made in which simultaneous exposure of two Fisher cells, one behind the other, were compared with two rectangular Corex-D.

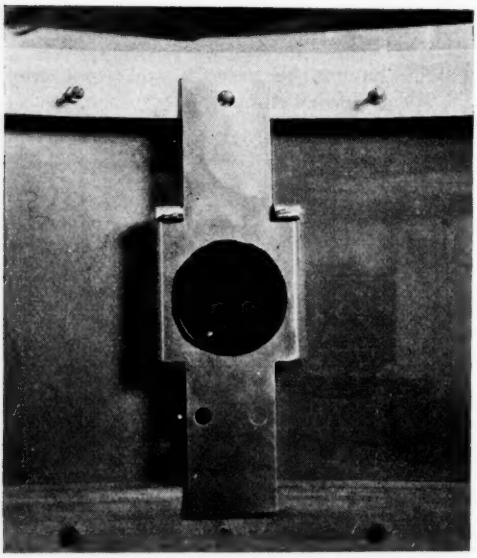


FIG. 5.—Circular quartz cell in holder on revolving frame of light-aging unit.

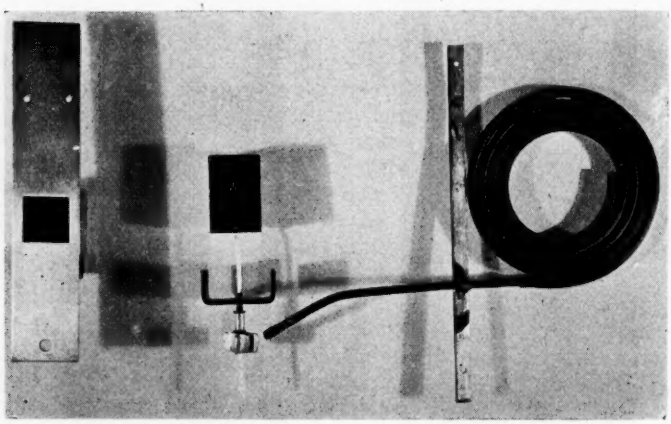


FIG. 6.—Rectangular Forbes quartz cell with stirring device—not assembled.

TABLE I

Type of aging unit	Eveready X-1	Atlas Weather-Ometer	Atlas Fade-Ometer
Distance from light source to specimen			
Inches	19.000	14.500	10.250
Meters	0.233	0.135	0.068
Actinometer rate cell only (Fisher) mg. per sq. dm. per min	6.51 *	1.88	5.60

* Actinometer rate based on "Sunshine" Carbons, Corex-D panels removed.

or quartz rectangular cells exposed side by side (Tables II and III). It will be noted that the decomposition of oxalic acid per square decimeter taking place in the second circular cell, is equivalent to 1.32 milligrams for industrial C carbons (Table II) and 1.50 milligrams for industrial U carbons (Table III).

Absorption experiments made by Forbes and coworkers in 1930 to 1934 indicate that light from 2,060 Angstrom units up to 3,132 Angstrom units is completely absorbed in a one-centimeter layer of solution so the light passing through the first Fisher cell probably consisted of wave lengths greater than 3,132 and less than 3,342 Angstrom units up to 4,700 Angstrom units. It thus appears that the use of one circular Fisher cell measures the intensity of light within approximately the desired range and as satisfactorily as is obtained in the "difference method", using filters. It is not the purpose of this brief article to set forth detailed data obtained in connection with the uranyl oxalate actinometer method, nor is it possible to show all of the detailed investigations which were made to confirm this.

A comprehensive study of the uranyl oxalate actinometer was made by C. E. Greider and F. T. Bowitch, of the Research Laboratory of National Carbon Co., Inc., in December, 1940. The following is quoted from this paper, by permission of these authors.

"The uranyl oxalate actinometer, with careful manipulation, will give very reproducible results with a constant source, and can be used as a method of evaluating the constancy of such a source. The use of the actinometer for the evaluation of short ultraviolet by a 'difference method' could not be made to yield constant results on account of the multiplication of errors arising from comparatively minor variations in the intensity of the source. The actinometer cannot be effectively employed to evaluate the difference between two sources of unlike energy distribution, unless the reaction for which the evaluation is desired has a spectral sensitivity substantially identical of that of the actinometer itself."

This finding confirms the conclusions which the writers had reached concerning this method.

The theory of the uranyl oxalate actinometer has been discussed at length by Dorcas and Forbes[21], by Anderson and Robinson[1], and arrangements by Bacon[4]. One of the writers[60] utilized this method in connection with the evaluation of the light stability of gasolines in petroleum oils. With the present standardized method, it is believed that accurate results can be obtained by using the Fisher circular cell, illustrated in Figure 4, by any laboratory operator who has no special training, provided, of course, that the standardization of solutions is carried out by an analytical chemist.

As far as the writers are aware, evaluation of sunlight aging had been carried out primarily by determining the degree of checking or the change in color and fading (see Figure 11)or various other visible changes, which were to say the least, subject to personal opinions. To place the evaluation of sunlight deterioration on a basis which would be more easily comparable and not subject to the personal equation, the suggestion was made to evaluate sunlight deterioration by measuring decrease in tensile strength or lowering of the percentage elongation, just as it is customary in evaluating oxidation and shelf aging. Figure 11 illustrates a special curved aluminum rack which is especially useful for testing matting and flexible decking.

The specimen holder, Figures 8 and 9, was developed for this purpose so that samples of rubber or synthetic rubber might be exposed to accelerated ultraviolet-light aging in any desired degree of extension.

TABLE II

SIMULTANEOUS EXPOSURES. TWO FISHER CELLS EXPOSED ONE BEHIND THE OTHER *vs.* TWO RECTANGULAR COREX CELLS EXPOSED SIDE BY SIDE

(See Figure 10 for apparatus)

Carbons: Industrial C
Ratios: $R_1 = \frac{C}{D}$ $R_2 = \frac{\text{Average Corex}}{c}$
Cells: Fisher C and D, Corex 1c and 2c
Exposure: 30 minutes

Exposure Number	Milligrams oxalic acid decomposed per sq. dm. per minute				Difference rectangular cells	R_1	R_2
	C	D	1c	2c			
40	3.21	1.46	5.38	5.63	0.25	2.20	1.71
41	3.31	1.32	5.75	5.75	0.00	2.50	1.74
42	3.21	1.29	6.37	6.62	0.25	2.49	2.02
43	2.90	1.20	4.89	—	—	2.42	1.69
44	2.85	1.08	5.32	5.14	0.18	2.64	1.84
45	3.04	1.24	6.00	5.70	0.30	2.45	1.92
46	3.50	1.36	5.81	—	—	2.57	1.66
47	3.50	1.41	6.25	—	—	2.48	1.78
48	3.11	1.32	5.81	5.87	0.06	2.36	1.88
49	3.35	1.20	—	5.56	—	2.79	1.66
50	3.59	1.41	6.25	6.37	0.12	2.55	1.76
51	3.49	1.46	5.75	5.63	0.12	2.39	1.63
52	3.40	1.44	5.75	5.75	0.00	2.36	1.69
Average of all exposures..	3.27	1.32	5.79		0.14	2.48	1.77

TABLE III

SIMULTANEOUS EXPOSURES. TWO FISHER CELLS AS IN TABLE II *vs.* TWO RECTANGULAR QUARTZ CELLS

(See Figure 10 for apparatus)

Carbons: Industrial U
Ratios: $R_1 = \frac{C}{D}$ $R_2 = \frac{\text{Average quartz}}{c}$
Cells: Fisher C and D, Quartz 1Q and 2Q
Exposure: 30 minutes

Exposure Number	Milligrams oxalic acid decomposed per sq. dm. per minute				Difference 1Q − 2Q	R_1	R_2
	C	D	1Q	2Q			
59	3.52	1.57	—	—	—	2.24	—
60	2.93	1.35	—	—	—	2.17	—
61	2.77	1.25	—	5.87	—	2.22	2.12
62	3.74	1.68	7.04	7.34	0.30	2.23	1.92
62A	3.26	1.37	6.36	6.49	0.13	2.38	1.97
63	3.59	1.58	6.30	6.49	0.19	2.27	1.79
64	3.76	1.77	7.34	7.10	0.24	2.12	1.92
65	3.19	1.37	6.12	—	—	2.33	1.92
66	3.45	1.68	6.98	6.98	0.00	2.05	2.02
67	3.17	1.44	—	—	—	2.20	—
70	—	—	6.61	6.49	0.12	—	—
72	—	—	6.43	6.43	0.00	—	—
73	3.03	1.42	—	—	—	2.13	—
78	3.44	1.47	—	—	—	2.34	—
Average	3.32	1.50	6.65		0.14	2.22	1.95

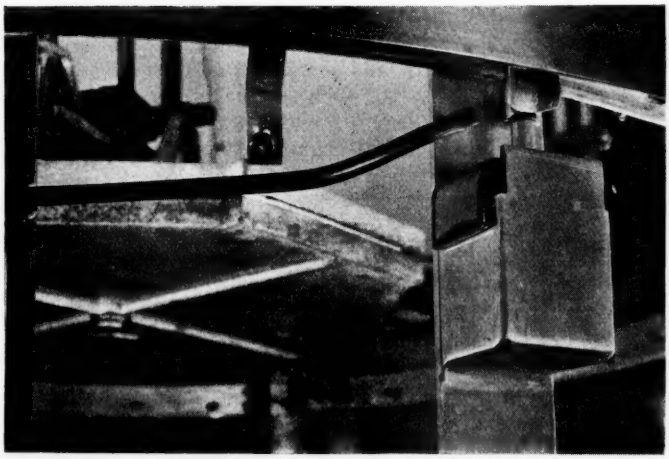


FIG. 7.—Rectangular quartz cell, with stirring device in holder on revolving frame of accelerated light-aging unit

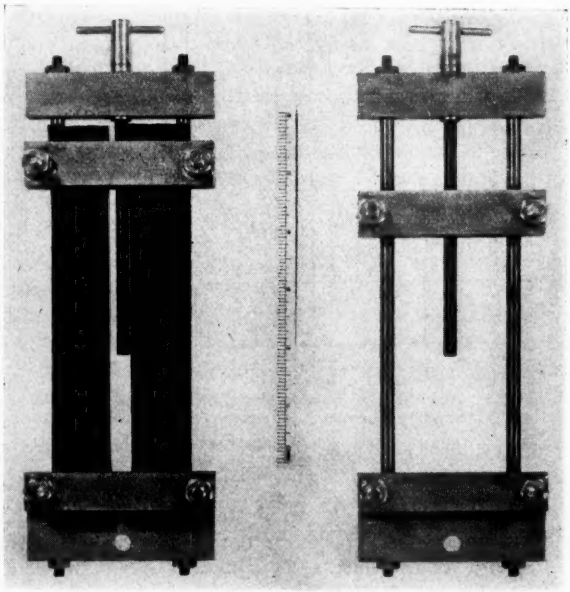


FIG. 8.—(*Left*) Specimen holder with sample; (*right*) without sample.

At first, dumbbell specimens were exposed in the sample holder, but it was soon found that the results were not reproducible because of "edge" effect. Entirely satisfactory results were obtained, however, when rubber slabs were exposed which were sufficiently large so that dumbbell specimens could be cut from them. Deterioration of tensile strength and loss of extensibility were in many cases noticeable long before visible effects, such as cracking or checking, could be detected. Apparently, therefore, deterioration of tensile strength and loss of elongation are forerunners of the usually recognized changes of cracking and checking.

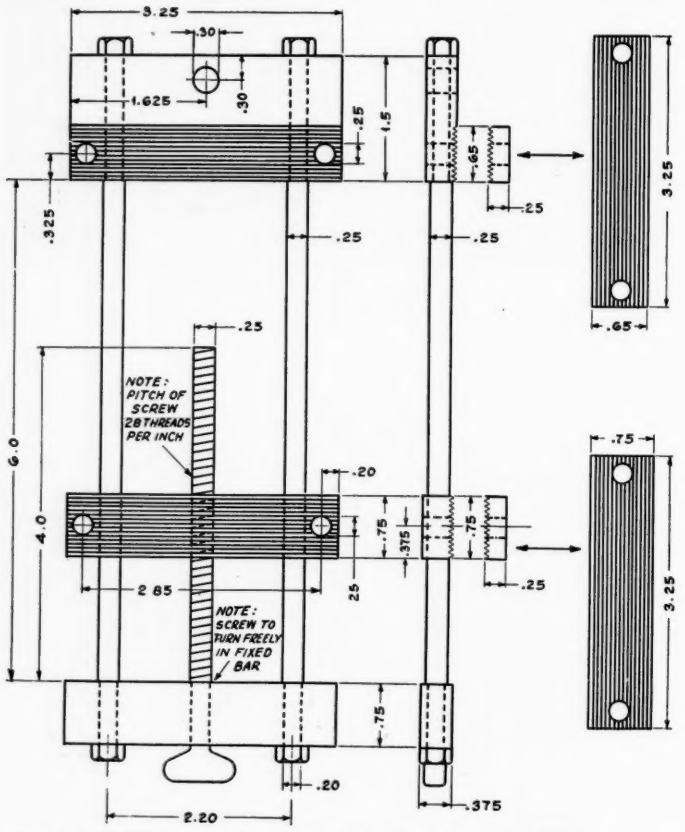


FIG. 9.—Detailed drawing of specimen holder for light aging. (All parts except rods made of aluminum; rods made of monel.)

It is difficult to draw any generally applicable conclusions, as the extent of deterioration will vary with the type of rubber compound or synthetic compound and with the thickness of the slab.

It should not be inferred from the above that the loss of tensile strength and decrease in extensibility are considered sole criteria of sunlight aging, because checking and cracking will no doubt remain necessary factors in evaluating weather and sunlight resistance. For specification purposes, it is particularly desirable, however, to include numerical figures as to permissible loss in tensile strength and decrease in elongation. With rubber stocks and some synthetics

the correlation between loss in tensile strength, determined by accelerated light aging on the one hand, and natural sunlight aging on the other hand, appears satisfactory. The loss in tensile strength of some rubber compounds, when exposed to sunlight, is very appreciable. Considerable additional work must be done to determine the advisability of exposure in an elongated condition, compared with exposure of samples at normal elongation. For example, in testing the light-resistance of certain rubber caulking compounds, it was found that this material showed remarkable resistance, both to accelerated aging and to sunlight-aging when stretched, compared to highgrade pure rubber compounds. The rubber caulking compound in question was compounded to have a high compression and to be somewhat thermoplastic. Exposure of this type of compound in sheet form while elongated indicated comparatively good resistance to sunlight, because sufficient cold flow apparently existed to prevent cracking. What makes an investigation of this sort interesting is that one always runs into the unexpected.

Materials subjected to either ultraviolet light in the accelerated-aging apparatus or to sunlight may behave in a manner entirely contrary to expectations. Thus a certain synthetic was compounded as a white stock, and light-aging tests were conducted which indicated that this white compound was several times as good, from the standpoint of light aging, as a carbon black compound. So the possibility exists that if this synthetic is produced in sufficiently large quantities, we may have the spectacle of white hose covers and completely white tires.

Another synthetic was found to have especially good resistance to ozone, yet showed particularly poor resistance to natural sunlight and to ultraviolet light exposure. This ought to be a challenge to the proponents of the theory that light-aging is a phenomenon which is caused solely by the presence of ozone.

The deterioration caused by ozone is, of course, well established and it is only meant to infer that light aging is a process which is not necessarily coupled up with ozone deterioration. The question of the action of ozone on rubber has repeatedly suggested the idea that light aging may be evaluated by measuring the resistance of rubber compounds to oxidation. Unfortunately, attempts to obtain correlation between resistance to oxidation, measured in the oxygen bomb or by the air bomb method, have not been found to be an indication of resistance to sunlight aging, so, if we require compounds which must resist weathering and sunlight, it will be necessary to continue to submit a compound to either natural sunlight aging or an accelerated light-aging test, such as that described. Work of considerable importance could be done by carrying out so-called "pure research" in determining sensitivity curves or various representative rubber compounds, as well as representative compounds of the several available types of synthetics.

This fundamental research could be undertaken to determine the light-response curve, or spectral sensitivity, of various representative types of rubber combinations by exposing such representative rubber in thin sheets to the radiation of measured quantities of essentially monochromatic light, and measuring some desirable physical properties, such as deterioration in elongation and (or) tensile strength. This work could be done only in a few exceptionally equipped laboratories, as it requires the use of an intense light source giving light of the range desired, a quartz manochromater, and thermocouple. The rubber would be exposed to this light for a definite period of time under controlled temperature conditions, and the light intensity would be measured by the thermocouple. By varying the wave length of the light, the maximum response to deterioration

could be ascertained for each type of compound, and entire region of response determined.

Manifestly, it is quite impossible to test each and every composition made commercially, since there are some four to five thousand commonly used rubber compounds, not to mention the number of rubber and synthetic rubber compounds which are used infrequently. It is suggested that this type of research work would be admirably suited as Ph. D. theses. How much more benefit they would be to the country as a whole than a thesis on "The use of the semi-colon in the St. James' version of the Bible."

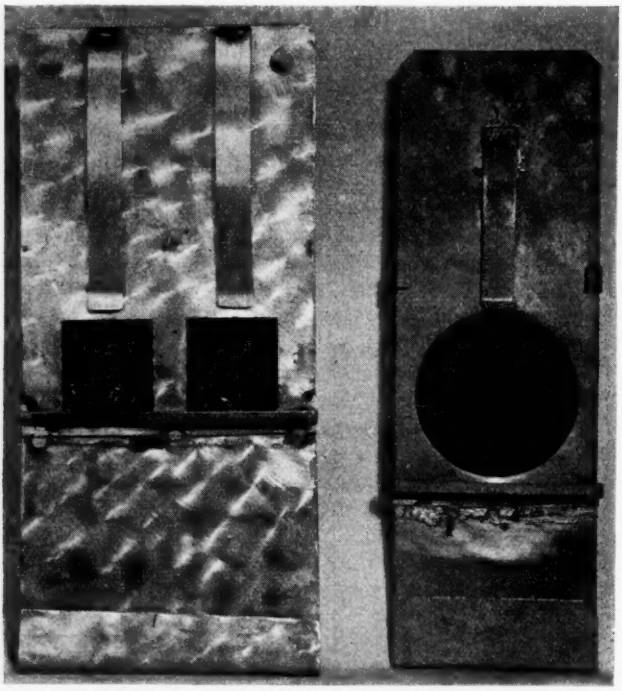


FIG. 10.—(*Left*) Dual holder for rectangular cells; (*right*) tandem holder for circular cells.

Supposing that this information were available, it would then be possible to select the ultraviolet light range of the aging lamp by the combined use of filters and selection of the proper carbons so that the rubber compound to be examined would quickly be evaluated in terms which could be directly converted to service life in average sunlight conditions.

As the deterioration of rubber and fabric dyes due to sunlight is apparently a photochemical reaction, it appeared logical to express this change in chemical terms, such as the decomposition of uranyl oxalate.

In unit time, sunlight exposure and accelerated ultraviolet exposure thus produced corresponding chemical changes, involving different quantities of chemicals per unit area of exposed surface. In view of the present growing importance of synthetic rubbers, it appears to be not at all unreasonable to expect that

synthetic rubber may be synthesized which will be sunlight-resistant by the nature of its atomic structural parts, rather than by physical compounding. The remarkable resistance of certain synthetics indicates that this is entirely feasible.

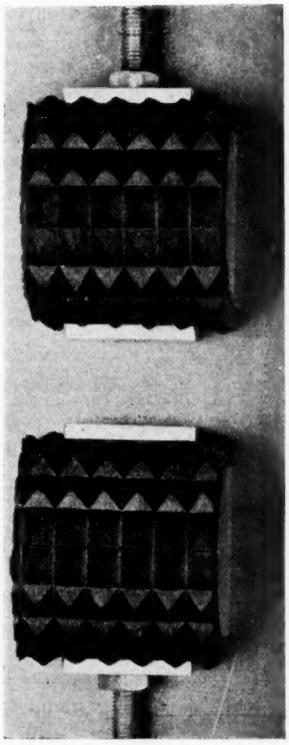


FIG. 11.—Curved aluminum rack for rubber-matting exposure tests.

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DETERMINATION OF FREE SULFUR IN VULCANIZED RUBBER *

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The following comments pertain to a paper of the above title by Mackay and Avons, published in *Transactions of the Institution of the Rubber Industry*, Vol. 16, pages 117-122, October 1940, and reprinted in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 14, pages 520-524, April 1941.

H. P. Stevens draws attention to the penultimate paragraph on p. 522 in which it is pointed out that the bromine method of oxidation is tedious and the reagent unhealthful, whereas perchloric acid may be dangerous. As a result of many years experience he is of the opinion that neither reagent is necessary. After adding nitric acid to the acetone extract in the flask, which should be covered with a watch glass, and when the reaction has subsided, about 0.5 gram of potassium chlorate is added and the mixture kept warm at 50 to 60° C. The top of a water oven is convenient; but the heating must be limited, as the yellow oxides of chlorine are rapidly driven off near 100°, and the liquid changes back from yellow to orange. The flask can be left to itself for an hour or two, but further addition of chlorate may be necessary to complete the oxidation. The contents are evaporated to dryness and taken up twice with concentrated hydrochloric acid preparatory to precipitation with barium chloride. A volumetric method may be preferable when a large number of routine tests have to be made, otherwise the final estimation can be made as barium sulfate.

In the second paragraph on p. 523, reference was made to long boiling with hydrochloric acid to decompose metallic sulfides. This is both inconvenient and unsatisfactory and, as stated, the sulfides are not completely decomposed. The specimen should be swollen in ether, and one or two cc. of concentrated hydrochloric acid added. The acid must not be in too large a proportion, as the specimen should be bathed in the ether and not in contact with the aqueous acid. As long as there is separation of aqueous acid in the bottom of the flask, there is sufficient. The specimen is allowed to soak and take up the acid with the solvent. Subsequent gentle warming completes the decomposition and expels the hydrogen sulfide liberated. A second treatment can be made and, if no hydrogen sulfide is evolved, decomposition of any metallic sulfides present is complete[1].

J. G. Robinson, interested in the comments on the method of Bolotnikov and Gurova, states that rejection of the direct aqueous sodium sulfide extraction in view of the previous unpublished work is not convincing, especially as the validity of this method had not previously been questioned and had, indeed, been confirmed by Oldham, Baker and Craytor[2]. The modification therefore only lengthens the method, without adding to its accuracy. He has used the original method of Bolotnikov and Gurova, and has found it rapid and reliable for checking routine production. It is true that the apparent free sulfur includes sulfur-bearing accelerators, but this is not of importance in routine checking where, after all, tests are made only to be certain that the apparent free sulfur does not rise above a predetermined value.

Recently he has made two small modifications to the original method. In the

* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 17, No. 2, pages 119-120, August 1941.

final titration he adds 10 cc. of formalin instead of 5 cc., and 30 cc. of 20 per cent acetic acid instead of 20 cc. The originally recommended quantity of formaldehyde was fairly closely balanced against the sulfite, and a slight error in measurement of the formaldehyde or the fact that the reagent has slightly deteriorated by standing would spoil the estimation. The excess formaldehyde and acetic acid does not interfere with the end point, but makes the method more foolproof.

J. G. Mackay states that the method detailed by Stevens is, of course, well known, and is in British Standard Specification No. 903 as an alternative to the bromine method. The authors did not, however, include this method in their study, because their express purpose was to obtain a rapid and accurate method for routine control-testing, involving a large number of determinations daily. With regard to Stevens' statement that when samples are known to contain metallic sulfides in large quantities, preliminary swelling with ether in the presence of hydrochloric acid is desirable, he found that a higher degree of accuracy does follow this preliminary extraction, but that, for rapid work within the limits necessary for works practice, such extraction could be omitted.

In reply to J. G. Robinson, he states that the authors decided to add a preliminary acetone extraction to the procedure described by Bolotnikov and Gurova because they do not think an aqueous solution of sodium sulfite "wets" rubber sufficiently to ensure complete reaction with free sulfur. In experiments on the determination of free selenium, they have found that refluxing with sodium sulfite for 30 hours does not remove all free selenium, although Cheraskove and Veisbrute[3] report that 100 cc. of 10 per cent sodium sulfite dissolves 0.1 gram of selenium after only 2 hours' boiling. Moreover, subsequent determination of the free sulfur present in the sodium sulfite solution following 30 hours' extraction yields only 93.4 to 94.5 per cent of the free sulfur found by other methods. Preliminary acetone extraction, therefore, seems a wise precaution. Provided that arrangements can be made for overnight extraction, little inconvenience is caused by the additional operation.

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IMPROVED SEMIMICRODETERMINATION OF SULFUR IN ORGANIC MATERIALS

PEROXIDE-CARBON FUSION FOLLOWED BY A TITRATION USING TETRAHYDROXYQUINONE INDICATOR *

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While investigating the *p*-toluenesulfonic acid esters of certain carbohydrates, it became desirable to develop a simple rapid method for the determination of 0.5 to 5 mg. of combined sulfur. The titration of sulfate ion with tetrahydroxyquinone indicator has acquired considerable prominence because of its rapidity[1, 2, 5-8, 10]; but has been used in conjunction with oxidation procedures which were often lengthy, usually required special equipment, or were unsuited to all types of compounds. The authors have found that the oxidation of sulfur in organic compounds to sulfate by sodium peroxide-carbon fusion, originally developed for the analysis of coal[3], may be satisfactorily combined with titration of sulfate ion with standard barium chloride solution, using tetrahydroxyquinone as an internal indicator.

The improved technique of Marvin and Schumb[4] was followed closely in the oxidation, and time was saved by using concentrated reagents in decomposing the fusion cake and in adjusting the pH of the resultant solution. The addition of a small amount of silver nitrate to the solution before titration was suggested by W. H. & L. D. Betz, Philadelphia, Penna., and has greatly increased the sensitivity of the indicator, making it unnecessary to subtract a titration blank. Common laboratory equipment was employed throughout, and duplicate estimations were within the accepted accuracy of the analytical balance and the 10-cc. buret used in the titration. Four analyses were ordinarily begun and completed in less than an hour.

MATERIALS AND REAGENTS

A mixture of 15 parts by weight of granular sodium peroxide and 1 part of 30- to 60-mesh sugar carbon, kept in a well-stoppered bottle.

Hydrochloric acid, 12 *N*, reagent grade.

Ammonium hydroxide, 16 *N*, reagent grade.

Barium chloride solution, 0.01 *N*, standardized gravimetrically by precipitation as barium sulfate; 1 cc.=approximately 0.0003 gram of sulfur.

Silver nitrate solution, approximately 0.1 *N*.

Ethyl alcohol, 95 per cent, denatured with 5 per cent methyl alcohol.

Phenolphthalein indicator, 1 per cent solution.

Tetrahydroxyquinone indicator, obtained from W. H. & L. D. Betz, Philadelphia, Penna.

Measuring dipper, capacity 0.15 gram of indicator.

* Reprinted from *Industrial and Engineering Chemistry*, Analytical Edition, Vol. 14, No. 1, pages 97-98, January 15, 1942.

TABLE I

DETERMINATION OF SULFUR

Sample	Wt. of sample (*mg.*)	Wt. of sulfur (calcd.) (*mg.*)	Sulfur (calcd.) per cent	Sulfur (found) per cent
p-Toluenesulfonyl chloride	22.8	3.84	16.8	16.8
	13.8	2.32	—	16.8
Sulfanilamide	23.5	4.37	18.6	18.6
	26.9	5.00	—	18.6
2,5-Dichlorosulfanilamide	17.8	2.37	13.3	13.3
	16.0	2.12	—	13.5
Sulfonal	10.0	2.81	28.1	28.1
	10.1	2.84	—	28.2
Thiourea	12.9	5.41	42.2	42.2
	12.2	5.14	—	42.3
Sulfur	2.71	2.71	100.0	99.8
	2.54	2.54	—	99.9
$C_{20}H_{28}O_{11}S$ (*p*-toluenesulfonic acid ester of erythrose derivative)	9.1	0.61	6.73	6.8
	17.7	1.19	—	6.8
Wool (air-dried)	20.3	1.22	5.91[a]	6.00
	30.3	1.82	6.13	6.00
Rubber (laboratory tubing, contained no zinc)	46.5	0.981	2.115[b]	2.11
	49.2	1.05	2.11	2.11
Rubber (laboratory tubing, contained zinc)	35.7	0.705	1.976[b]	1.98[d]
	39.6	0.783	1.977	2.00
Mineral oil	45.3	0.49	1.09[c]	1.10
	48.4	0.53	—	1.13
Mineral oil	89.4	0.627	0.701[b]	0.71
	87.3	0.610	0.699	0.71

[a] Determined by Carius analysis.
[b] Determined by method of Waters.[9]
[c] Determined by A. S. T. M. method D-129-39.
[d] Zinc removed by method of Sheen, Kahler, and Cline.[8]

PROCEDURE

The sample, containing 0.5 to 5 mg. of sulfur, was weighed into a 30-cc. nickel crucible and covered with approximately 6 grams of the fusion mixture. The crucible was supported in a vessel so that its lower half was cooled by a current of cold water. A fuse, made by impregnating cotton string with potassium nitrate, was inserted part way into the charge. Combustion was carried out by igniting the fuse and promptly covering with a nickel lid. Too vigorous oxidation could be avoided by increasing the sodium peroxide content of the fusion mixture. On cooling, the fusion cake was broken, removed by rapping the crucible sharply, and placed in a 250-cc. Erlenmeyer flask with 10 cc. of 12 *N* hydrochloric acid. The flask was covered with a watch glass until the vigorous reaction subsided. Hot aqueous washings of the crucible, its cover, and the watch-glass were added, with a few drops of phenolphthalein. The solution was boiled 5 minutes to destroy peroxides, adding, if necessary, more hydrochloric acid to maintain the acidity. The solution was cooled slightly and made just alkaline with 16 *N* ammonium hydroxide. Boiling was resumed to remove excess ammonia until the color of the

indicator was permanently discharged. The volume of the solution was adjusted to approximately 25 cc.

After cooling to room temperature, 25 cc. of alcohol, 0.1 gram of tetrahydroxyquinone indicated ($\frac{2}{3}$ dipper), and 2 to 3 cc. of 0.1 *N* silver nitrate were added, and the mixture was shaken until the indicator dissolved. The cloudy yellow solution was titrated very slowly with the standardized barium chloride solution, with vigorous shaking throughout. When all the sulfate had been precipitated, the presence of excess barium ions was denoted by a permanent pink coloration of the solution. The end point could be readily detected by observing the change in color of the particles of silver chloride under artificial illumination. The presence of precipitated salts, carbon, or large amounts of chloride ion did not affect the end point when determined in this manner.

The unpracticed eye may have severe difficulty in accurately detecting the end point of the titration. False indications of an end point are often given by the color change to pink in the bulk of the solution and on the surface of any sodium chloride precipitates. The true end point is given by the appearance of a pink coloration on the flocculent silver chloride coagulum, which settles more slowly than sodium chloride, and is best viewed as a cloud of suspended particles by transmitted artificial light. It is often advantageous to add a few more drops of silver nitrate solution toward the end of the titration. The authors are indebted for these observations to Thomas S. Gardner, whose results entirely support their claims concerning the accuracy and reproducibility of the method.

The data in Table I show that the estimation of sulfur gave satisfactory results with a variety of pure compounds containing sulfur combined in different ways, and that the figures for wool, zinc-free rubber, and mineral oil agreed with those obtained by standard procedures. Zinc, as it occurred in rubber, interfered with the titration, but was conveniently removed after the peroxide-carbon fusion by the method of Sheen, Kahler, and Cline[8]. The method has been applied to the analysis of a large number of *p*-toluenesulfonic acid esters of partly ethylated carbohydrates. In the following typical series, the percentage of sulfur is given first as directly determined and second as calculated from a single ethoxyl analysis: 2.50, 2.45; 2.84, 2.84; 2.90, 2.90; 3.01, 2.97; 3.10, 3.03; 3.21, 3.13; 3.22, 3.17; 3.25, 3.30; 3.30, 3.30; 3.57, 3.42; 3.70, 3.65; 3.74, 3.80; 3.90, 3.92; 4.04, 3.92; 4.25, 4.15; 4.79, 4.65; 5.22, 5.20; 5.32, 5.30; 5.41, 5.40. An average variation of 1.9 per cent between the two values was obtained.

SUMMARY

Sulfur combined in a variety of nonvolatile organic compounds was oxidized to inorganic sulfate by a sodium peroxide-carbon fusion, and the sulfate ion was estimated by titration with standard barium chloride solution, using tetrahydroxyquinone as an internal indicator. No special apparatus was required, and 0.5- to 5-mg. quantities of combined sulfur were determined with speed and accuracy. The method should be especially useful for the routine analysis of materials like oil or rubber, with modification, if necessary, to remove interfering ions, and is apparently general for all types of sulfur-containing substances, including sulfonic acid derivatives.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of W. H. & L. D. Betz in providing unpublished procedures for the determination of sulfur with tetrahydroxyquinone, and of C. B. Purves, A. A. Morton, G. G. Marvin, and A. G. Assaf.

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DETERMINATION OF ZINC IN RUBBER COMPOUNDS

A NEW INTERNAL INDICATOR METHOD *

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A survey of the chemical literature reveals very little information regarding the determination of zinc in rubber compositions. Some of the earlier standard procedures involve the use of the gravimetric sulfide method, but the only direct references to the use of ferrocyanide as a volumetric precipitant with an external indicator applied to the analysis of rubber compounds are those of the A. S. T. M.[1] and Casazza[3]. The A. S. T. M. method is used in the rubber industry with various modifications and, in the absence of evidence to the contrary, is assumed to be the only volumetric method in general use for the determination of zinc.

The difficulty of manipulation and the low degree of accuracy of the external indicator procedure led to the consideration of a new method for this determination. The principal internal indicator methods for the determination of zinc have been considered by Kolthoff and Furman[7]. One method employs ferrocyanide as precipitant and ferrous iron as an indicator, and the other, based on the work of Cone and Cady[4] supplemented by that of Kolthoff[6], utilizes the ferricyanide-ferrocyanide oxidation-reduction system in equilibrium with precipitated zinc potassium ferrocyanide, using diphenylamine or diphenylbenzidine as indicator. With the latter method as a basis, the experimental work for the development of a procedure suitable for the analysis of all types of rubber compounds was undertaken.

EXPERIMENTAL

With some modifications the diphenylbenzidine indicator method proved satisfactory in the presence of the ions usually found in an acid solution of the ash obtained from rubber compounds. It was also successful with rubber compounds of certain simple types, if the ash was treated in such a manner as to remove all oxidizing agents, reducing agents, and iron, if chlorides were present in only small quantities, and if there were no more than 10 grams of ammonium salts present in the solution to be titrated.

However, when this method was applied to the analysis of rubber stocks containing clay or other silicates, the zinc found was from 10 to 30 per cent low. This observation apparently has not been reported in the literature. Investigation of this phenomenon revealed that it occurs with any method of analysis which involves ashing as a preliminary step because of a reaction between zinc oxide and silicates which occurs even at the lowest possible ashing temperature. The reaction product is not decomposed by ordinary acid treatment and even prolonged acid digestion gives results 5 to 10 per cent low. The presence of lead oxide also causes low and inconsistent results, but the reasons for this effect have not been investigated yet.

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Because of these phenomena it became necessary to resort either to fusion or to wet oxidation (digestion) to find a generally applicable method for the preliminary destruction of the sample. The latter method is the more practical. Concentrated nitric acid, bromine, and fuming nitric acid, used successively, will oxidize most of the organic material in a rubber compound. The best reagent for oxidizing the carbon black and organic substances remaining in the residue is perchloric acid, and when its addition is preceded by the above oxidizing agents, this reagent is safe to use. Unfortunately, even small quantities of perchlorates had a detrimental effect on the color change and position of the end point when diphenylamine or diphenylbenzidine was used as indicator. Since no way of overcoming this effect was found, it became necessary to discontinue the use of these indicators in connection with wet-oxidation methods of determination.

Because of these facts, it was necessary to devise a new method suitable for determining zinc after wet oxidation of the sample. Gravimetric methods were discarded as impractical. Precipitation methods, such as precipitation with anthranilic acid or 8-hydroxyquinoline, followed by volumetric determination of the precipitate, were discarded as time-consuming and none too accurate in solutions containing as many ions and added salts as are inevitably present. The problem centered on finding a suitable indicator to be used with the ferricyanide-ferrocyanide system in the manner of diphenylbenzidine.

Only indicators from stock which were thought to possess oxidation potentials in the neighborhood of +0.75 volt were tried. The results obtained indicated that the potential of a suitable indicator must be no higher than +0.75 volt and probably not much lower. The compounds which proved to be unsatisfactory in color development or in reproducibility of end point were *p*-phenetidine, benzidine acetate, *N*-phenylanthranilic acid, p-aminodiphenylamine, 2,4-diaminodiphenylamine, diphenylcarbazide, and two *p*-phenylenediamine derivatives. All these indicators were tried under varying conditions of temperature and acidity, both by direct and back-titration. *p*-Anisidine showed promise as an indicator, but proved to give very high results. *o*-Tolidine gave satisfactory results, but the color change, yellow through yellow-green to blue-green, was not sharp enough to ensure accuracy without considerable experience.

Schulek and Rózsa[10] described a new multiform indicator, *p*-ethoxychrysoidine, which presumably had the properties desired for this purpose, although the literature does not describe this use for it. A sample of this dye was prepared as described below, and it was found to be an excellent indicator under at least two sets of conditions applicable to the analysis of rubber compounds.

Tananaev and Georgobiani[11] reported the use of "blue ethyl acidic RR(B)", 2-(*p*-ethylaminophenylazo)-1,8-dihydroxynaphthalene-3,5-disulfonic acid sodium salt, as an indicator for lead titration with ferrocyanide, and suggested its use for the determination of other metals. According to Rowe's Colour Index[9], Ethyl Acid Blue RR(B) is dye No. 59, which is the sodium salt of *p*-dimethylaminobenzeneazo-1,8-dihydroxynaphthalene-4-sulfonic acid. This was available from Eimer & Amend, New York as Azo Acid Blue B, originally obtained from G. Grubler and Co., Leipzig. This dye was not received until the work described below was completed, but it was then tried as a substitute indicator. The end point was not quite so sharp as with *p*-ethoxychrysoidine, and the results were somewhat erratic, but further work on conditions of operation might prove it to be a satisfactory indicator.

As a result of the experimental work, two methods of analysis were devised and tested. Method I is the more general, and is, with slight modification,

applicable to all rubber compounds, vulcanized and unvulcanized, and to latices. Method II is applicable only to rubber stocks and latices free of lead, silicates, or other fusible ash, and containing but small amounts of acid-insoluble fillers.

METHOD I. WET-OXIDATION METHOD

Reagents and Solutions

Indicator.—*p*-Ethoxychrysoidine (*p*-ethoxyphenylazo-*m*-phenylenediamine), 0.2 per cent in sulfuric acid (sp. gr. 1.84, diluted 1 to 1 with water). The indicator is prepared by coupling diazotized *p*-phenetidine hydrochloride with *m*-phenylenediamine. An analogous preparation for chrysoidine is described by Houben-Weyl[5]. Recrystallization of the dye is unnecessary. Store the solution in darkness.

Standard potassium ferrocyanide solution.—Approximately 0.04 *M* solution of reagent grade potassium ferrocyanide trihydrate. If available, highly purified crystals may be used as a primary standard, but the solution is not stable (cf. standardization).

Standard zinc chloride solution.—Zinc solution (0.06 *M*) made from zinc of known purity, dissolved in hydrochloric acid, or impure zinc compound dissolved in acid and standardized against potassium ferrocyanide (cf. standardization).

Potassium ferricyanide.—One per cent of the reagent grade crystals dissolved in water. This solution is stable only if kept in darkness.

Nitric acid-bromine mixture, reagent grade nitric acid (sp. gr. 1.42), saturated with bromine. Free bromine must be present.

Perchloric acid, reagent grade, 60 or 72 per cent acid.

Sulfuric acid, reagent grade (sp. gr. 1.84) diluted 1 to 1.

Ammonium hydroxide, reagent grade (sp. gr. 0.90).

Wash solution, 25 grams of ammonium sulfate and 10 cc. of ammonium hydroxide per liter.

Fuming nitric acid.—The red fuming type is preferred. Reagent grade.

Procedure A (For Vulcanized Rubber Compounds Only)

Place the ground sample of rubber (0.5 to 2.0 grams) in a 400- to 500-cc. wide-mouthed flask. Add 15 cc. of nitric acid-bromine mixture, cover the flask, and let stand for 10 minutes or longer. Add 10 cc. of red fuming nitric acid, replace the cover, and place on a steam plate or bath until the rubber is disintegrated. Transfer to an electric hot plate or a burner, remove the cover, and evaporate to 10 to 15 cc. Cool partially, add 10 cc. of perchloric acid, and evaporate until all carbon and organic material are destroyed.

(*Caution.*—To ensure safety to the operator, the operations involving the oxidation of organic substances with perchloric acid should be done behind a safety screen. The evaporation of perchloric acid to fumes should be done under a hood whose flue is free from condensed organic vapors, organic dust, and carbon or soot.)

This operation requires a temperature of about 200° C. Continue evaporation to about 5 cc. Dense white fumes should be evolved, and the hot solution may be pale yellow, but should become colorless on cooling unless much iron is present. If lead is present, add 3 cc. of sulfuric acid, and evaporate until dense fumes again appear.

Dilute to 50 cc., boil one minute, cool, neutralize with ammonium hydroxide, add 5 cc. in excess, and boil one minute. Filter hot and wash with four 25-cc.

portions of hot wash solution. For greater accuracy, when there is a large flocculent precipitate, wash only twice with 20-cc. portions of wash solution, wash the precipitate into the original flask, add 5 cc. of sulfuric acid, digest, precipitate as before, filter, and wash the precipitate with four 20-cc. portions of wash solution. Evaporate the combined filtrates to 100 to 125 cc., making sure in every case that nearly all of the ammonia is boiled off to prevent the formation of excess ammonium salts. Add 5 cc. of sulfuric acid, and titrate in the manner described below. The temperature must be 90° C at the start of the titration, and should not fall below 70° C.

Add 4 to 6 drops of indicator and 4 to 7 drops of ferricyanide solution, the latter always in amounts equal to or greater than the former. Shake until the red color changes to yellow, and titrate with standard ferrocyanide solution until a strong salmon-pink color persists. Back-titrate with standard zinc solution to pale green. Continue "back-and-forth" titration (as few times as possible) until a few drops of zinc solution cause the color to fade through a neutral shade to very pale apple green. The last few drops must be added slowly, with shaking between drops, since the precipitation equilibrium is reached slowly. Because of the equilibrium conditions, the zinc must always be added last. When only small quantities of zinc are present the indicator may not fade readily on addition of ferrocyanide. This may be remedied by adding several cc. of zinc solution first.

Standardization.—If the zinc solution is a primary standard, standardize the ferrocyanide with it according to the method just described, using a hot solution containing the zinc, 5 cc. of sulfuric acid, and 5 grams of ammonium sulfate per 100 cc. of solution. If the zinc solution is not standard, standardize the ferrocyanide with 0.1 *N* potassium permanganate according to the method of Kolthoff and Furman[8]. This method specifies that about 1 gram of ferrocyanide in 120 cc. of 1 *N* sulfuric acid be titrated with permanganate, and that a fresh, approximately 1 per cent ferricyanide solution be used for color comparison at the end point. The ferrocyanide solution may also be standardized against permanganate or ceric sulfate, with *o*-phenanthroline-ferrous *complex* (ferroin) as indicator. The zinc solution can then be standardized against the ferrocyanide solution.

Procedure B (For Latices and Unvulcanized Rubber Stocks)

Because of the difficulty of destroying unvulcanized rubber readily with nitric acid-bromine mixture to such an extent that the use of perchloric acid is safe, the following modification of Procedure A is necessary.

Add 20 cc. of nitric acid-bromine mixture to the sample of latex or thinly sheeted unvulcanized rubber compound and warm until vigorous reaction starts, keeping the flask covered. If overnight digestion is convenient, add 20 cc. of red fuming nitric acid after the first reaction has subsided, cover the flask, and allow it to stand overnight on a steam plate or bath. After this treatment, perchloric acid may be added and the evaporation safely continued, as in Procedure A. If the determination must be completed without interruption, add 10 cc. of red fuming nitric acid after the first reaction has subsided, heat gently until the rubber is disintegrated, and evaporate nearly to dryness. Add 10 cc. of red fuming nitric acid and 10 cc. of perchloric acid, and evaporate as in Procedure A. Whichever method of digestion is used, complete the determination according to Procedure A. The actual rubber content of samples should not exceed 2 grams. Do not evaporate or coagulate latices before the oxidation.

METHOD II. ASHING METHOD

This method may be used for unvulcanized and vulcanized compounds and latices which contain no clay or lead, and have a comparatively low acid-insoluble ash.

Reagents

Same as in Method I where specified with the addition of reagent grade hydrochloric acid (sp. gr. 1.2), saturated bromine water, and 1 per cent diphenylbenzidine in concentrated sulfuric acid.

Procedure A (*p*-Ethoxychrysoidine as Indicator)

Ash a sample of from 0.5 to 2.0 grams of rubber in a crucible in an overnight ashing muffle furnace which is capable of slowly ashing the sample without combustion at a maximum temperature of 550° C. Ashing may be accomplished over a burner if the sample is not allowed to flame.

Treat the ash with 5 cc. of hydrochloric acid and 5 cc. of sulfuric acid, warm if necessary to free the precipitate from the crucible, and transfer to a beaker. Dilute to 50 cc., boil to dissolve all the ash possible, add 5 cc. of bromine water, cool, neutralize with ammonium hydroxide, and continue the preparation of the solution and the determination exactly as in Method I, Procedure A, except that the solution must be boiled for at least 10 minutes after acidification before titration.

Procedure B (Diphenylbenzidine as Indicator)

Up to the point of adding the indicator, follow Method II, Procedure A, exactly. In place of *p*-ethoxychrysoidine add 4 drops of diphenylbenzidine and 4 to 5 drops of ferricyanide solution. If a deep blue color does not develop, add sulfuric acid in 2-cc. portions until it does appear on shaking. Titrate with ferrocyanide solution until the blue fades markedly to gray-green, stop titrating, and shake with the addition of small portions of sulfuric acid until a deep purple color appears; then continue dropwise titration to yellow-green. Back-titration is permissible, but the ferrocyanide must be added last.

DISCUSSION OF METHODS

Indicators

The use of *p*-ethoxychrysoidine may require some experience in determining the best ratios of indicator to ferricyanide. When there was much variation in this ratio from that specified in the procedure, the accuracy was affected to a small extent, because the equilibrium between the ions from the precipitate, the ferrocyanide ions from reduced ferricyanide, and the excess ferrocyanide ions necessary to reduce the indicator is sensitive to variations in the quantities of indicator and ferricyanide. Because of this equilibrium, and because of the greater sharpness of the end-point color change, the titration must be finished with the zinc solution.

Since the diphenylbenzidine method checked well with electrometric titration and also with the *p*-ethoxychrysoidine method in standardization titrations, Method II, Procedure B, may be used as a standard to check experimental work with *p*-ethoxychrysoidine. However, the author found that *p*-ethoxychrysoidine end points were better than those obtained with diphenylbenzidine because the

latter indicator fades during titration and it is frequently difficult to bring the color back sufficiently to obtain a sharp end point.

In standardization with diphenylbenzidine indicator, 5 grams of ammonium sulfate and 5 cc. of sulfuric acid per 100 cc. of solution must be present. More sulfuric acid usually must be added during titration, as noted in Method II, Procedure B.

Neither indicator works well with less than 10 mg. of zinc, but standard zinc solution may be added to the reaction mixture as soon as there is evidence of too little zinc in the solution.

The use of ferricyanide incorporated in the standard ferrocyanide solution as advocated by Kolthoff and Furman[7] was not satisfactory with either indicator.

Interferences

Oxidizing and reducing agents which affect the ferricyanide-ferrocyanide system or the indicator interfere with both methods, but all such substances are removed by the preliminary treatments. Manganese and copper interfere, but they are not usually found in rubber compounds except those containing certain organic copper rubber dyes. Any other metals which form precipitates with ferrocyanide in strong acid solution interfere, with the exception of lead, which is successfully removed by Method I but not by Method II. Results of trial determinations of mixtures containing lead indicate that there should be no more than a slight positive error when using Method I, even if some lead sulfate is present at the time of titration. About 5 grams of chloride ion can be present in Method I, and about 3 grams in Method II, without impairing the end-point colors. Ammonium sulfate must be present for quantitative precipitation, but amounts greater than 10 grams tend to diminish the intensity of the end-point colors.

Iron must be removed if present to an extent great enough to cause a very noticeable blue color when ferrocyanide is added. A very small trace of iron appears to sharpen the end-point colors, but most rubber compounds contain too much iron to leave in the solution. A number of substances which form complex ions with ferric iron were employed in an attempt to eliminate the removal of iron. Tartrate, citrate, oxalate, fluoride, phosphate, and pyrophosphate were without effect, although the last was cited by Aruina[2] as being effective for this purpose.

Applications

In addition to being applicable to practically all rubber stocks and latices, the method will probably be equally effective with synthetic rubber mixtures which do not contain appreciable quantities of saturated hydrocarbons. Organic zinc compounds can be readily determined by either method. Inorganic zinc compounds can be determined by titration of an acid solution of the material, using either indicator if interfering ions are removed. Application to alloys would be more difficult because of the necessity of removing interfering ions present and added during preliminary treatment. The removal of interfering ions by precipitation with hydrogen sulfide is not recommended because drastic treatment, such as evaporation with percholic acid, would be necessary to remove the excess hydrogen sulfide, traces of which are very injurious to the determination. The determination of smaller quantities of zinc by means of a more dilute ferrocyanide solution, a larger sample, or both, is now being investigated.

DISCUSSION OF RESULTS

The precision and accuracy of the titrations of standard zinc solution were tested by a series of comparisons of the *p*-ethoxychrysoidine method with the diphenylbenzidine method and with electrometric titration. The diphenylbenzidine end point coincided with that obtained with electrometric titration within ±0.2 per cent. The precision obtained in five successive titrations, using diphenyl-

TABLE I

RESULTS OF A STUDY OF THE METHODS

Sample No.	Per cent zinc oxide present	Per cent zinc oxide found, average	Precision, average per cent deviation from mean, ±	Accuracy, per cent deviation of mean from true value
EXTERNAL INDICATOR METHOD, URANYL ACETATE ON SPOT PLATE				
1[a]	4.20	4.59	1.3	+ 9.3
2[a]	4.17	3.52	6.0	—15.6
3[a]	4.65	3.40	3.0	—27.0
4[a]	21.10	19.50	2.5	— 7.6
METHOD II, PROCEDURE B, USING DIPHENYLBENZIDINE				
1[a]	4.20	4.08	1.0	— 2.8
2[a]	4.17	3.12	4.0	—25.0
2[b]	4.17	3.30	9.0	—21.0
3[a]	4.65	3.82	2.3	—18.0
3[b]	4.65	3.90	2.5	—16.0
4[a]	21.10	20.75	0.96	— 1.7
4[b]	21.10	20.90	0.38	— 0.95
METHOD II, PROCEDURE A, USING *p*-ETHOXYCHRYSOIDINE				
1[a]	4.20	4.16	0.40	— 1.0
4[b]	21.10	21.03	0.10	— 0.3
6[b]	2.75	2.44	3.50	—12.7
METHOD I, PROCEDURE A				
1[a]	4.20	4.17	0.54	— 0.7
2[a]	4.17	4.18	0.70	+ 0.2
2[b]	4.17	4.22	0.20	+ 1.2
3[a]	4.65	4.45	0.75	— 4.3
3[b]	4.65	4.52	0.70	— 2.9
4[a]	21.10	20.70	0.50	— 1.9
4[b]	21.10	21.10	0.10	0.0
5[b]	2.30	2.28	0.44	— 0.9
6[a]	2.75	2.74	0.91	— 0.3

[a] One precipitation of ammonia-insoluble material.
[b] Two precipitations of ammonia-insoluble material.

benzidine, was ±0.2 per cent average deviation from the mean. The average of twenty successive *p*-ethoxychrysoidine titrations was the same as that of the diphenylbenzidine titrations, and a precision of ±0.2 per cent was obtained with a maximum deviation of ±0.5 per cent. In this last series of titrations the ratio of indicator to ferricyanide was varied through all combinations from 4 to 6 drops of indicator and from 4 to 7 drops of ferricyanide in which the ferricyanide was present in amounts equal to or greater than the indicator. When ratios outside these limits were used, the values obtained were more erratic, but still had a precision within ±0.5 per cent.

Table I shows the results of analysis of specially prepared rubber compounds by the uranyl acetate indicator method[1] and by Methods II-B, II-A, and I-A. The experimental compounds were carefully weighed and mixed in 500- and 1000-gram batches. The quantities of zinc oxide added and the batch weights were carefully checked. The purity of the zinc oxide used was 100 ± 0.2 per cent, determined by analysis according to a simplified form of Method I-A. The compounds were vulcanized in the form of sheets, $6 \times 8 \times 0.1$ inches, and samples from various parts of the sheets were ground together for analysis. The experimental compounds contained the following principal fillers:

1. 21 per cent carbon black
2. 21 per cent whiting, 21 per cent clay, and 10.5 per cent titanium dioxide
3. 23 per cent barytes and 23 per cent clay
4. 21 per cent whiting, 10.5 per cent magnesium carbonate, and 2.5 per cent ferric oxide
5. 31 per cent barytes and 18.5 per cent clay
6. 16.5 per cent carbon black and 11 per cent litharge

The results tabulated in Table I show very clearly the effect of ashing on the accuracy of zinc determinations in rubber compounds containing clay or lead. The data leave little choice between the accuracy and precision of Methods I and II, providing lead and clay are absent. The poor results obtained with the external indicator method are difficult to explain, and may not be typical of the method, although difficulty has frequently been encountered in this laboratory with regard to obtaining the same type of end point in the determination as in the standardization. The amount of reagent used for a blank with the external indicator method is large and inconsistent.

To test Method I further, results obtained in routine analysis in the laboratory over a period of several months were examined for precision. Only those determinations in which two or more analyses were run were considered in compiling the averages. Eighteen samples, varying from 1.2 to 6.1 per cent in zinc oxide content, were analyzed with a precision (average percentage deviation from the mean) of ± 1.14 per cent and a maximum single deviation from the mean of 2.60 per cent. Seven other samples containing from 14.0 to 45.0 per cent zinc oxide were analyzed with a precision of ± 0.31 per cent and a maximum single deviation from the mean of 0.85 per cent.

A test of Method I, Procedure B, was made involving eight successive determinations of zinc oxide in a latex mix. The average value was 1.97 ± 0.9 per cent. This is satisfactory precision when it is considered that obtaining a homogeneous sample of a latex mix as heavily compounded as the one used in these tests is not always easy. It was found that, ordinarily, not more than two samples could be taken from a latex mix without thoroughly remixing the batch to maintain homogeneity.

To summarize the interpretation of the data obtained in testing these procedures: Any of the internal indicator methods described is capable of accuracy and precision sufficient for most analyses for research in rubber technology, and is also well suited to the speed required in control analyses, without appreciable loss of accuracy. Each method, however, must be used only under the conditions most favorable to its success.

A comparison of the merits of the methods by analysts in this laboratory resulted in a general preference for Method I over the external indicator method. No comparisons with Method II were made by the analysts, but the author's

experience has been that titration with *p*-ethoxychrysoidine as indicator by either method is more rapid than titration with diphenylbenzidine. The back-titration necessary when *p*-ethoxychrysoidine is used is of advantage when small or unknown quantities of zinc are present, and there is no uncertainty concerning the approach of the end point, as there frequently is with diphenylbenzidine. With diphenylbenzidine, the return of the purple color before final titration to an end point is frequently slow, and the speed of color return appears to be a function of the proximity to the end point when titration is interrupted, and to the quantity of sulfuric acid in the solution.

SUMMARY

Two internal indicator volumetric methods for the determination of zinc in rubber compounds have been devised and investigated. The first method is a wet-oxidation method employing nitric acid, bromine, and perchloric acid as oxidants, and *p*-ethoxychrysoidine, a new oxidation-reduction indicator for this use, as indicator. It is of general application to all types of rubber compounds. The second method, less generally applicable to rubber compounds, utilizes either the new indicator or the well-known indicator, diphenylbenzidine. This method depends on ashing of the sample, and cannot be used for the analysis of zinc in rubber compounds containing lead or silicates, since it has been found that no method in which the sample is ashed yields accurate results if these substances are present. Both methods use potassium ferrocyanide as the volumetric precipitant and potassium ferricyanide as an integral part of the indicator system. Both methods are applicable to other organic and inorganic zinc-containing materials. The first method appears to have a slight advantage in ease of manipulation, total time of determination, and range of applicability. There is little choice between the methods or indicators as regards precision, accuracy, or the actual time used by the analyst for a determination, providing each method and indicator is used only under the proper conditions. Both methods are superior to the external indicator method using uranyl acetate, the method now in common use in rubber laboratories.

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THE ECONOMICS OF THE USE OF NEOPRENE RECLAIM*

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Every rubber chemist or compounder is, by the nature of his profession, an economist. One of his most important duties, if not the most important duty, is to produce, at the lowest possible cost, articles which will have adequate and satisfactory performances in service. With synthetic rubbers, which cost three or four times as much as natural rubber, extra efforts must be made to keep compound costs at a minimum. The inescapable cost of mould scrap, and the inexcusable cost of scorched or set-up stocks resulting from improper or careless processing or scheduling, must be considered as parts of the overall compound cost. Unless care is exercised to avoid scorched stocks, the overall factory cost of an article may be increased considerably over the estimated cost, thus vitiating an otherwise successful development, promotion, and sales campaign. The ability of a compounder may be judged by the size of the scrap pile, but at least the cost penalty of scorched stocks can be partially decreased by salvaging or reclaiming these unfortunate errors. It is the purpose of this paper to discuss ways and means of salvaging scorched stock, with particular reference to vulcanized and partially vulcanized Neoprene stocks.

COST REDUCTION METHODS

With the current increase in production and shortage of synthetic elastomers, the reclamation of scrap is of pertinent interest as a conservation as well as an economical measure. In England, where there is no domestic source of elastomers, the situation has become so critical that recently the Ministry of Aircraft Production has approved the use of up to 25 per cent of reclaimed Neoprene in Neoprene stocks[1]. Fortunately the situation in this country has not reached, and possibly may not reach, such a stage, but cognizance should be taken of the familiar adage—"To be forwarned is to be forearmed."

It is obvious that the cost of a Neoprene compound may be reduced by:

(1) diluting or extending the Neoprene with natural rubber or rubber reclaim.

(2) diluting the Neoprene with fillers and (or) softeners.

(3) diluting or extending the Neoprene with ground Neoprene scrap or Neoprene reclaim.

The first method is of questionable overall economy, because those physical properties of the product which demand the use of Neoprene suffer in direct ratio to the proportion of rubber or rubber reclaim used. In addition, commonly used rubber accelerators, necessary for vulcanizing the rubber hydrocarbon phase of the mixture, frequently function as powerful accelerators of Neoprene, and this results in set-up or scorching of the unstable mixed stock. The obvious solution to this problem is to blend Neoprene and rubber stocks immediately before final processing or curing, but such a procedure results in extra handling

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and consequent extra cost, and may defeat the economy of adding the rubber or rubber reclaim to the Neoprene.

The use of additional fillers and softeners is the practice usually adopted in reducing the cost of a compound. The use of additional proportions of softeners allows the use of more filler to maintain a given hardness after curing. These additions alter the physical properties of the vulcanizate, so ultimately a compromise must be made between the desired physical properties and compound cost.

The third method is one which is now coming into prominence. The reclamation of cured scrap is of almost as great importance economically as the reduction of cured scrap. Heretofore the quantity of Neoprene scrap accumulated by an individual manufacturer has been of such a small volume as to render special handling of it uneconomical. With more and more Neoprene being used, it is desirable, both from an economic and conservation viewpoint, to devise a method of reusing Neoprene scrap.

REUSE OF NEOPRENE SCRAP

One far-sighted reclaim manufacturer has initiated a long-range research program with a view to determining methods of reclaiming Neoprene and other synthetic elastomers. Although it does not seem possible to "devulcanize" and reclaim Neoprene by the same means and in the same sense as rubber is reclaimed, Neoprene can be reused by one of the following methods.

(a) Bin-cured or set-up stocks can be replasticized to usable plasticity by softeners (tri-*o*-tolyl phosphate or other esters) and (or) chemical plasticizers (Latac or Accelerator-552). The use of chemical plasticizers is applicable only to Neoprene Types G and GN, and is very efficient with these types of Neoprene if bin cure has not reached an advanced stage.

(b) Cured scrap or set-up stock can be ground on a tight mill and added to the compound as "ground springs". This method has been adopted almost universally with varying degrees of success as a means of disposing of an otherwise embarrassing scrap situation. As may be realized, such ground scrap should be screened before use, and should be added only to those compounds in which quality is subordinated to cost.

(c) Cured scrap may be converted into a pseudo-reclaim by grinding on refiner mills, and adding physical softeners so that a thin sheet may be plied up on the refining roll. Depending on the composition of the scrap and the reclaimer's particular process, this method produces a reclaim similar in appearance to rubber reclaims. At present, most reclaim manufacturers are prepared to custom reclaim Neoprene scrap. In essence, this method is similar to the first method, except that fully cured scrap (mould scrap) can be used because of the better grinding action of refining mills, compared to conventional rubber mills.

A method of mill reclaiming Neoprene scrap which has been used with some success is[2]:

"The scorched material is broken down on a conventional rubber mill or refining mill. To the shredded material is added, in small increments, approximately 5 per cent, by weight on the Neoprene, of a wetting agent (mixed sodium salts of sulphated cetyl and oleyl alcohols). Each increment is thoroughly incorporated before the next addition is made. This is continued until a smooth unbroken sheet is obtained. The addition of 1-5 per cent of process oil, tricresyl phosphate, or raw Neoprene aids in the reclaiming. The addition of 1 per

cent of naphthalene to the reclaim after it has aged overnight assists in subsequent processing."

The remainder of this paper will be devoted to a discussion of the economies of using so-called Neoprene reclaim, prepared on refining mills by reclaimers.

ANALYSES AND PROPERTIES OF RECLAIMS

Since Neoprene reclaims are produced on a custom basis, considerable variation is to be expected in samples obtained from various sources, because there are no standard types of Neoprene reclaim in the same sense that there are standard types of rubber reclaim.

A quantity of Neoprene tire-tread scrap (trimmings and mould flash) of the following composition was accumulated:

Neoprene Type GN	100
Latac	0.25
Stearic acid	1
Neozone-D	1
Extra-light calcined magnesia	4
Channel black	31
Circo light process oil	1
Zinc oxide	5

The tread scrap was custom-reclaimed by a prominent reclaim manufacturer, and is identified as Reclaim E. At the same time samples of Neoprene reclaim were solicited from four other reclaim manufacturers. These are identified as Reclaims A, B, C, and D in Table I, which shows the analysis and the mill behavior of each reclaim.

TABLE I

ANALYSIS OF NEOPRENE RECLAIMS

Reclaim	Chlorine (percentage)	Sulfur (percentage)	Acetone extract (percentage)	Ash (percentage)	Specific gravity	Neoprene (percentage)
A	13.88	0.50	10.94	16.37	1.476	37.9
B	14.06	3.05	15.29	25.08	1.481	38.0
C	9.83	1.29	22.92	9.23	1.386	26.6
D	10.19	2.33	26.02	9.82	1.395	27.5
E	19.00	0.96	25.73	5.04	1.306	51.4
Tread stock	25.60	1.28	5.59	4.57	1.392	69.3

APPEARANCE ON THE MILL

Reclaim

A—Sample ran slightly rough on mill—neutral odor.

B—Sample too rough and short to form band on mill. Pronounced odor of factice and (or) dibenzyl ether.

C—Sample ran satisfactorily on mill—similar to inner tube rubber reclaim. Odor of cumarone and (or) rubber reclaim.

D—Sample ran slightly rough on mill. Pronounced odor of naphthenic acids or naphthenates.

E—Sample ran satisfactorily on mill—neutral odor.

The chlorine determinations were made by the Parr bomb method[3] and are a necessary part of a Neoprene reclaim analysis to assay the Neoprene content of the reclaim. Commercial Neoprene contains an average of 37 per cent chlorine. This factor was used in calculating the Neoprene content of the reclaims shown in Table I.

Speculation on the probable composition of the reclaim, or the compound from which the reclaim was made, is rendered easier by reconstructing the previous table, so that the analysis is based on 100 parts (by weight) of Neoprene. This has been done in Table II.

TABLE II

ANALYSIS OF RECLAIMS BASED ON 100 PARTS (BY WEIGHT) OF NEOPRENE

Reclaim	Sulfur (percentage)	Acetone extract (percentage)	Ash (percentage)	Total parts by weight less 100 parts neoprene
A	1.3	28.9	43.1	164
B	8.0	40.1	66.0	163
C	4.9	86.1	34.7	276
D	8.5	94.7	35.7	264
E	1.8	50.1	9.8	95
Tread stock	1.8	8.1	6.6	44

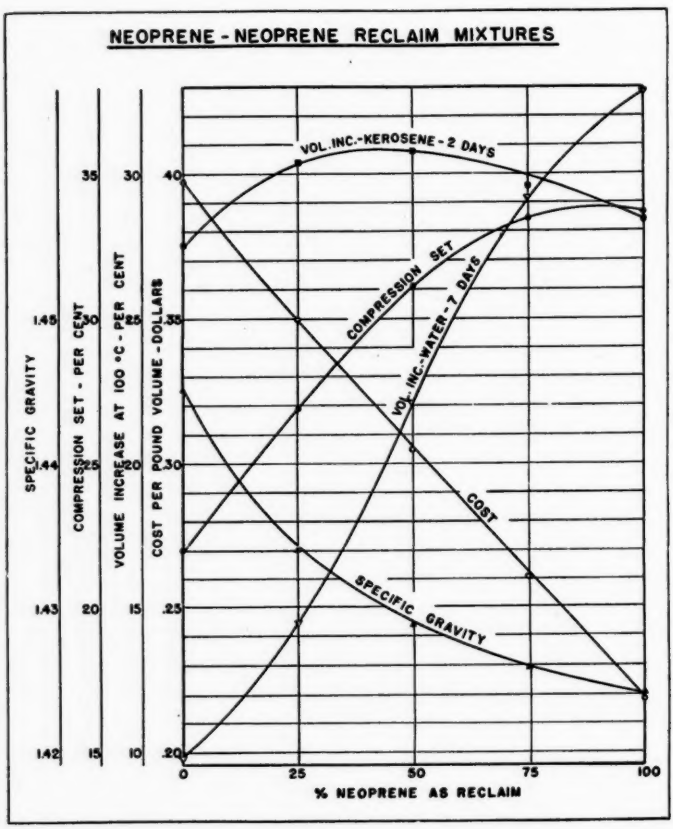

FIG. 1.

The analyses indicate that, because of the high ash figures, Reclaims A to D contain substantial proportions of whiting, clay, or barytes. Reclaims B, C, and D probably contain factice, as indicated by the high sulfur content, and large proportions of acetone extractable material as well, as by the low hardness (Table III).

In addition to differing in composition, the reclaims differed in physical properties. Table III shows the stress-strain results obtained on slabs press-cured 40 minutes at 307° F. Also shown are the results after the reclaims were compounded with 10 parts of extra-light calcined magnesia and 10 parts of zinc oxide per 100 parts by weight of reclaim.

TABLE III

STRESS-STRAIN RESULTS

(Press cure—40 minutes at 307° F)

Reclaim	Stress at 300% elongation	Tensile strength (lbs. per sq. in.)	Elongation at break (percentage)	Shore hardness
UNCOMPOUNDED				
A	425	425	300	65
B	200	500	530	31
C	200	325	500	40
D	250	350	460	43
E	175	500	400	38
COMPOUNDED WITH 10 MgO — 10 ZnO				
A	...	475	275	75
B	200	600	575	42
C	325	425	450	59
D	400	475	360	65
E	525	700	360	52

Compounding with magnesia and zinc oxide has only a slight effect on the stress-strain results, although the Shore hardness is considerably increased. This indicates that, in Neoprene-Neoprene-reclaim mixtures, no allowance should be made in the accelerator (metallic oxide) content for the Neoprene hydrocarbon in the reclaim.

SUBSTITUTING RECLAIMED NEOPRENE FOR CRUDE NEOPRENE

With this background, a series of tests was conducted to determine the effect on cost and physical properties of substituting Neoprene reclaim for crude Neoprene in an arbitrarily chosen compound. For this work, Reclaim E, made from the known tread stock scrap, was chosen. The data in Table II indicate that, in reclaiming the cured tread stock, the reclaimer added to the Neoprene scrap 42 parts of acetone extractable material per 100 parts of Neoprene. Allowing for some error in the analytical results, it was assumed that actually 50 parts of softener had been used.

A series of compounds was then mixed and tested. In this series, the compounds were identical except that different amounts of raw Neoprene were replaced by an equivalent amount of Neoprene contained in the Neoprene reclaim. The stock containing all crude Neoprene was identical with the original tire tread compound except that 50 parts of a coal-tar derivative were added to

compensate for the softener added to the reclaim during the refining operation. In addition, the total carbon black content was increased by the addition of soft carbon black to 100 parts to obtain stiffer and more millable stocks. The same amount of carbon black was also added to the reclaim alone. The actual stocks tested and the cost figures of the stocks are shown in Table IV.

In milling the compounds, the Neoprene was first plasticized with Latac, and then blended with the reclaim before further compounding. In calculating the compound costs, the market prices appearing in the August, 1941, issue of the *India Rubber World* were used. The price of the reclaim was assumed to be 20 cents per pound. The usual price of custom reclaiming is 10-15 cents per pound. To the higher figure was added 5 cents per pound to compensate for shipping and handling costs.

Using these compounds, several conventional tests were made. The results (on the 40-minute at 307° F cure unless otherwise noted) are shown in Table V.

The cost figures in Table IV show that the cost of the particular compound used may be reduced 20-25 per cent by replacing half of the raw Neoprene with

TABLE IV

NEOPRENE—NEOPRENE-RECLAIM MIXTURES

Raw Neoprene: Reclaim Neoprene.	100:0	75:25	50:50	25:75	0:100
Neoprene Type-GN	100	75	50	25	—
Reclaim E.	—	48.5	97	145.5	194
Latac	0.25	0.1875	0.125	0.06	—
Stearic acid	1	0.75	0.50	0.25	—
Neozone-D	1	0.75	0.50	0.25	—
Extra-light calcined magnesia	4	3	2	1	—
Channel black	31	23.25	15.5	7.75	—
Soft carbon black	69	69	69	69	69
Circo light process oil	1	0.75	0.5	0.25	—
Bardol-B	50	37.5	25	12.5	—
Zinc oxide	5	3.75	2.5	1.25	—
Cost per lb.	$0.275	$0.244	$0.214	$0.183	$0.154
Cost per lb. (vol.)	$0.397	$0.350	$0.305	$0.261	$0.219
Specific gravity	1.445	1.434	1.429	1.426	1.424

Neoprene hydrocarbon in the form of reclaim. The compounds chosen may be used for medium- or low-grade mechanical goods, such as grommets, dust seals, automotive bushings, etc., which are generally used in a static condition in service. Such compounds would be unsuited for high-grade mechanical goods subjected to severe flexing or abrasion.

In Table V the plasticity-recovery figures were determined by the Williams' parallel plate plastometer, under a load of five kilograms. The plasticity number is the thickness in thousandths of an inch of a two-cubic centimeter pellet after three minutes at 80° C, the pellet being heated for 15 minutes at 80° C before testing. The recovery is the increase in thickness one minute after removal from the plastometer. The lower the figure, the softer and more plastic the stock. The plasticity figure of the 50:50 mixture indicates that it would be suitable for most factory operations, including tubing. With ratios of reclaim higher than this, the stock would be too rough and nervy for easy processing.

The presence of reclaim up to 75 per cent does not adversely affect the original stress-strain properties or aging in the air pressure-heat test. In fact, in the aging test, judged by the greater retention of elongation and less increase in hardness on aging, the presence of reclaim is advantageous.

Resilience is reduced and the compression set is increased as the reclaim content increases. The compression set was determined according to A.S.T.M. Designation D-395-40T, Method B, under 30 per cent deflection, except that pellets ¾-inch diameter by ½-inch were used.

TABLE V

TEST RESULTS

Raw Neoprene	100	75	50	25	0
Reclaim Neoprene	0	25	50	75	100
1. *Plasticity-recovery at 80° C of compounded stock*	61-1	106-4	200-51	320-99	333-125
2. *Stress-strain results—original*					
Cure at 307° F (min.)	20	20	20	20	20
Stress at 200% elongation	375	300	325	325	325
Tensile strength (lbs. per sq. in.)	1,100	1,150	1,250	1,075	625
Elongation at break	495	490	500	460	290
Shore hardness	55	54	51	51	53
Cure at 307° F (min.)	40	40	40	40	40
Stress at 200% elongation	425	400	375	375	300
Tensile strength (lbs. per sq. in.)	1,100	1,150	1,250	1,075	625
Elongation at break	420	420	440	430	290
Shore hardness	55	54	53	53	53
Cure at 307° F (min.)	80	80	80	80	80
Stress at 200% elongation	450	425	425	325	325
Tensile strength (lbs. per sq. in.)	1,125	1,175	1,325	1,075	675
Elongation at break	400	410	460	420	300
Shore hardness	56	54	54	53	53
Aged 20 Hours at 260° F — 80 #/In.² Air Pressure (Air Pressure-Heat Test)					
Cure at 307° F (min.)	40	40	40	40	40
Stress at 200% elongation	1,025	1,175	750	600	450
Tensile strength (lbs. per sq. in.)	1,025	1,175	1,225	1,175	1,025
Elongation at break	100	100	200	200	220
Shore hardness	90	86	82	78	74
3. *% Resilience under 20% compression*	59.6	55.5	50.7	51.2	52.5
4. *Compression set (30% deflection)*	22.0	26.9	31.1	33.5	33.5
5 *Volume increase (percentage)*					
Kerosene at 100° C					
2 days	27.5	30.4	30.8	29.6	27.6
Water at 100° C					
7 days	9.8	14.5	22.1	29.2	32.9
14 days	21.4	30.1	42.1	42.5	47.3
Process oil at 82° F					
7 days	2.8	5.5	7.0	7.1	7.6

The volume increase in kerosene is not greatly affected by the presence of reclaim, but the water absorption increases proportionately as the reclaim is increased.

For ease in comparison, some of these data are plotted in Figure 1.

SUMMARY

It is possible to reclaim mould and other vulcanized Neoprene scrap by suitable reclaiming procedures. At the present time, most of the reclaim manufacturers are prepared to do this reclaiming on a custom basis. The Neoprene of the reclaim may replace as much as 50 per cent of raw Neoprene in a compound

to reduce by as much as 25 per cent the volume cost, without greatly impairing the physical properties of medium-or low-grade mechanical goods vulcanizates. Use of Neoprene scrap in this manner will conserve the supply of Neoprene, and under present conditions the value of such conservation is obvious. Besides, this utilization of scrap will reduce the overall factory cost of many types of Neoprene products.

Although the volume of Neoprene scrap available at the present time is small, the presence of larger amounts on the market, as a result of increased Neoprene production, must be anticipated. Because of increased interest in Neoprene reclaims, due attention should be given to the problem of classifying and standardizing types of Neoprene scrap and reclaim.

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[3] Parr, *J. Am. Chem. Soc.* **30**, 764 (1908).

ELECTRICAL PROPERTIES OF CONDUCTIVE RUBBER

INCLUDING A RECOMMENDED METHOD OF TEST FOR DETERMINING ELECTRICAL CONDUCTIVITY OF RUBBER *

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The electrical properties of conductive rubber cannot be expressed completely in terms of specific resistance alone. Determinations based on the measured resistance, R, of a homogeneous sample of the rubber placed between metallic electrodes, when substituted in the equation for the specified resistance:

$$\rho = R\frac{A}{l} \qquad (1)$$

give results which vary between very wide limits for different values of the cross-sectional area, A, perpendicular to the lines of current flow, and of the length, l, of the conductive path parallel to the lines of current flow. From the nature of the relation between the observed results and the magnitudes of A and of l, it appears that there is a resistance of considerable magnitude at the boundary between the metallic electrode and the conductive rubber. That such a high contact resistance does, indeed, exist may be verified by simple experiments. To describe or to specify adequately the performance of conductive rubber, it becomes essential, therefore, to be able to evaluate separately both this contact resistance and the internal, or inherent, resistivity of the material.

The internal resistivity may be determined directly by conventional methods. A known current, sent through a sample of the conductive rubber between current electrodes making contact with its surface at the ends of a strip having uniform cross-section perpendicular to the lines of current flow, causes a potential drop, along a given length, which is proportional to the internal resistance of that length of the sample. This potential drop may be measured by electrodes placed on the surface between the current electrodes and making contact along lines of right angles to the lines of current flow. The arrangement of the circuits for this measurement are shown in Figure 1.

By using a potentiometer, which, at the balance point, permits no current to flow through the potential electrodes, the existence of any contact resistance between these electrodes and the material is without effect on the determination. The ratio of the measured potential drop to the known current is, in this case, the true internal resistance of the length of the sample between the potential electrodes. The *internal resistivity*, ρ, in ohms per unit cube, is then obtained by

* Reprinted from *The Rubber Age* (New York), Vol. 50, No. 3, pages 203-205, December 1941. At the Forty-Fifth Annual Meeting of the National Fire Protection Association, held in Toronto, Canada, May 12-16, 1941, a report was submitted by the Association's Committee on Gases. This report contained recommendations concerning the adoption of electrically conductive rubber in the manufacture of various products exposed to electrostatic hazards, such as those which exist in operating rooms. An appendix to the report provided a standard method for testing the electrical conductivity of rubber. The complete report of the Committee on Gases has been tentatively adopted by the N.F.P.A. for the next year. That portion of the report dealing with the testing of rubber to determine its electrical conductivity, a subject which is receiving much attention these days, is reproduced.

multiplying the resistance thus computed by the ratio of the cross-sectional area, A, of the sample at right angles to the lines of current flow to the length, l, of the sample between the potential electrodes, as in Equation (1).

Unfortunately no such simple method is available for the determination of the contact resistance. If we were justified in assuming that the internal resistance was independent of the orientation of the material, we might compute the contact resistance for both faces as the difference between the total resistance between electrodes placed on opposite faces and the internal resistance of the material between these faces. This would involve determining the internal resistivity for a rectangular parallelepiped of the material by the method just described and then measuring the total resistance between electrodes placed on opposite faces. The

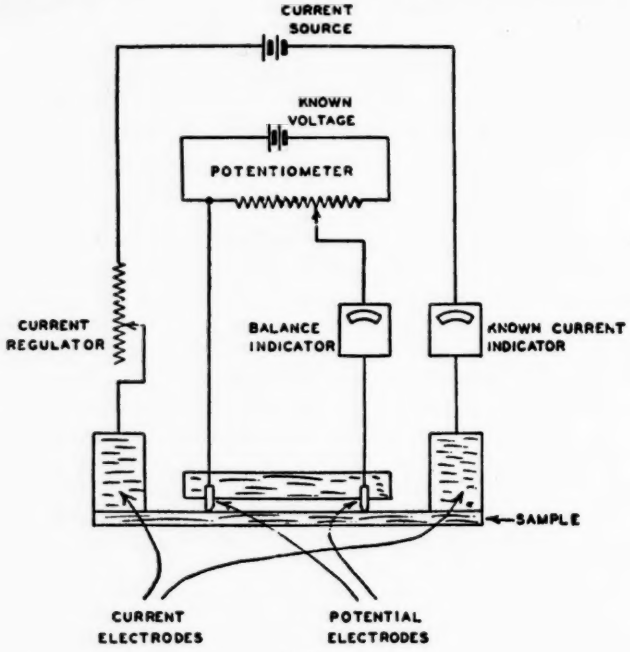

FIG. 1.

lines of current flow in these two cases, are, however, at right angles to each other, and there is no assurance that the internal resistivity determined for one case is correct for the other.

The contact resistance can, however, be determined indirectly from measurements made with a single arrangement of four electrodes on a homogeneous sample of the material having the form of a rectangular parallelepiped. Let a current electrode be placed in contact with one surface of this rectangular parallelepiped at one end, covering the surface for a distance, D, from the end. Let the inner edge of the electrode make contact with the surface along a line perpendicular to the lines of current flow as current passes from this electrode to a similar electrode similarly placed at the other end of the sample. Both electrodes should be in contact with one surface of the test-piece, as shown in Figure 1, and the lines of current flow in the main body of the material should be parallel to this surface. The resistance between one metallic electrode and a plane through

its inner edge, perpendicular to the lines of current flow, depends on both the contact resistance between the electrode and the conductive material and on the internal resistance of the material. This follows from the fact that current entering the sample at a distance from the inner edge of the electrode must pass first through the contact resistance of a narrow strip parallel to the edge and then through the internal resistance of the length between this strip and the edge.

The whole sample may, in fact, be considered as an electrical network, as shown in Figure 2, made up of many very small current paths, the resistance of some being due to the contact effect at the surface and of others to the internal resistance of the material. This contact resistance may be expressed as g, the surface conductance in mhos per unit length of sample parallel to the line of

TABLE I

ELECTRODE LENGTH—B CM.

Values of rg	Values of R/r	Values of rg	Values of R/r
0.0006	833.	0.40	1.86
0.0010	500.	0.60	1.41
0.0015	334.	1.0	1.04
0.0025	201.	1.5	0.829
0.0040	125.	2.5	0.634
0.0060	84.0	4.0	0.501
0.010	50.7	6.0	0.408
0.015	33.9	10.	0.316
0.025	20.6	15.	0.258
0.040	13.2	25.	0.200
0.060	9.00	40.	0.158
0.10	5.63	60.	0.129
0.15	3.96	100.	0.100
0.25	2.63		

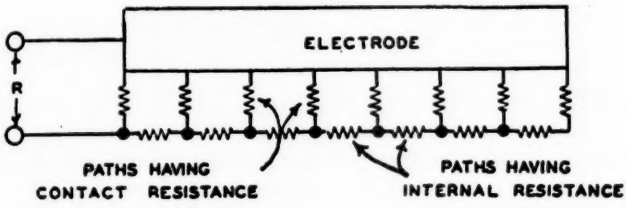

FIG. 2.

current flow. This internal resistance may be expressed as r, the resistance in ohms per unit length of sample parallel to the lines of current flow. This latter value may be determined as previously described.

The effective resistance between the electrodes and planes through their inner edges may be determined by measuring the total resistance between the two electrodes and subtracting the resistance, due to that portion of the sample included between the planes. The total resistance, Rr, between the electrodes may be determined, by means of the circuits shown in Figure 1, by transferring the connections of the potentiometer to the current electrodes and measuring the total potential drop in the same manner as that used for determining the internal resistance. The resistance of the material between the two inner edges of the electrodes and parallel to the lines of current flow may be computed as the product of the resistance per unit length, r, and the distance, D, between

these inner edges. The resistance, R, under a single electrode may be considered as being $\frac{1}{2}$ of the electrode resistance. In other words:

$$R = \frac{R_T - rD}{2} \qquad (2)$$

We, therefore, have a value for R, the resistance between one electrode and the plane through its inner edge, and a value for r, the internal resistance per unit length of the sample. The problem now is to determine the value of g, the surface conductance per unit length.

It is difficult to express g explicitly in terms of the two known resistant values. It is possible, however, to compute values of the ratio R/r for a number of assumed values of the product rg, taking into account the length of the particular electrode used in the measurements, measured parallel to the lines of current flow. These values may be plotted against each other, preferably on logarithmic graph paper. We may, therefore, compute the ratio R/r from the available data, look up the corresponding value of rg on the chart, and divide the latter by the known value of r to obtain the desired value of g. From this we may obtain the *surface conductivity* G, in mhos per unit area, by dividing g by the width of the sample.

Representative values for the two quantities, R/r and rg, are given in Table 1. In computing these values, the length of the electrode parallel to the lines of current flow was assumed to be 2 cm.

In practice it has been found convenient to use a test piece 10 cm. long and 2 cm. wide, cut from a sheet sample of the material. Grease and other foreign matter should be removed from the surface by wiping lightly with a cloth moistened with acetone. Suitable current electrodes may be made from blocks of brass 2 cm. wide and weighing 400 gm. each. Placed one on each end of the strip, they extend in for 2 cm., cover an area of 4 sq. cm. each, and exert a pressure of 100 gm. per sq. cm. The potential electrodes may be bars of brass 1/16 in. thick set parallel to each other in slots in a block of nonconductive material so that they are maintained at a fixed separation of 10 cm. The general arrangement of electrodes and sample is shown in Figure 1. Accuracy in placing the electrodes may be assured by extending them over the sides of the sample and locating them by means of pins fixed in a nonconducting base.

The electrical connections are shown diagrammatically in Figure 1. All readings of voltage magnitudes are made by means of a calibrated scale on the potentiometer.

For conductive materials in the form of thin sheeting, particularly when such sheeting is not homogeneous but contains a fabric or other nonconductive insert, the resistance effective to current flowing longitudinally through the sheeting, *i.e.*, parallel to the surface, is particularly significant. This property may be evaluated most conveniently in terms of the resistance of a portion one centimeter long of a strip of the sheeting one centimeter wide. This may be termed the *longitudinal resistivity* of the material. Like the internal resistivity, it must be evaluated independently of any surface contact effects. Its value may be obtained quantitatively by multiplying r by the width of the sample, in the same way that surface conductivity was obtained from g by dividing by the width. Although there is no conventional unit for this property, numerical values may be expressed in terms of ohms per centimeter square.